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Remediation of contaminated land and solutions with binders derived from waste material

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Abstract

Metal leaching behaviour was investigated in synthetically prepared soils which were contaminated with lead in the laboratory and to which ordinary Portland cement (OPC), lime, magnesia, fly ash (PFA),or ground granulated blast furnace slag (GGBFS) were added to stabilise the contaminant. The optimum amounts were determined by fly ash added gradually to contaminated soil until full reduction of leachable lead was reached.

Five grams of the soil thoroughly mixed with 0.1g stabilising material was transferred into a 100ml polypropylene container to which 50ml of de-ionised (DI) water or 50 ml of 0.1M HNO_3 or 0.01M HNO_3 was added. The mixture was shaken on a flat bed shaker for 2 hours, and then filtered using a Whatman No 542 filter paper. The lead concentration in the filtrate was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES).

All theses stabilizers resulted in about 99% of the added lead being retained on the filter. However, in similar experiments with 0.1M HNO_3 effective lead retention was found only when OPC or GBFS were used where amounts retained were 90 and 95% respectively. The effect of changes in pH on lead retention was investigated using Raman Spectroscopy, X-ray Diffraction (XRD), Fourier Transformation Infrared Spectroscopy (FTIR), Raman Spectroscopy and Scanning Electron Microscopy (SEM) and X-ray photo spectroscopy (XPS) and ion chromatography.

In a second series of experiments Lead contaminated solutions containing 10, 50, 100, and 500 mg/l, respectively of Pb were treated by the addition of known quantities of OPC, lime, magnesia, GGBFS or fly ash. The resulting lead-containing precipitate was collected and characterised using XRD, FTIR, Atomic emission Spectroscopy ICP-AES, SEM-EDX , Raman and XPS. Analysis of the supernatant by Inductively Coupled Plasma Spectrometry showed that about 99% of lead in solution was removed after the addition of 0.1g of OPC, lime or magnesia, PFA, or GGBFs to the 50ml of lead solution. Characterisation of the cement treated samples showed the formation of $PbCO_3$, $PbSO_4$ and $PbSiO_3$. The addition of lime resulted in the formation of $Pb2OCO_3$, $PbSiO_3$, $PbCO_3$ and $Ca(PbO_3)_2$. In the presence of magnesia, the following compounds were formed: Mg_2Pb, $PbMgV_2O_7$ and PbO_2. Results from both IR and SEM-EDX confirmed the presence of lead in the precipitate.

When deionised water or 0.1M HNO_3 was used in the presence of GGBFS, the concentration of lead in the leachate was less than 1% of the added lead in the soil. Results from X-ray diffraction measurements on soil samples retained on the filter paper showed lead calcium silicate and a mixed compound of lead sulphate carbonate hydroxide were formed in the presence of GGBFS.

These investigations show that the addition of cement, lime or magnesia, GGBFS and PFA can result in the removal of lead from the solution to form stable compounds, thus providing a potential means of clean-up of solutions contaminated with lead.

In addition to the work on contamination with lead, contamination with seven other elements was also investigated: Zn, Pb, Cd, Cr, Cu, Ni, Al. The levels of the concentration of the solution were varied: 10, 50, 100 and 500 mg/l.

The solidification procedures were applied with 20,000 mg/l of Pb solution on cube shape 50×50 ×50mm samples that were cured for 7 days. Then tank leaching test was conducted on solidified samples together with an acid digestion test. This work was extended to the examination of the leaching behaviour of the compounds formed by subjecting lead contaminated OPC cubes (50x50x50mm), cured for 7 days, to leaching in a tank of DI water. Results showed that less than 1% of the lead had leached out within 15 days. In addition, similarly treated cubes with varying amounts of OPC replaced with fly ash or GGBFS were subjected to the leaching tank and compressive strength tests. The results of the tests showed better retention of Pb where OPC was replaced by PFA or GGBFS.

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Chapter one

General introduction

1.1. Background

The Department of the Environment Transport and the Regions (DETR) consider that between 50-100,000 sites in the UK may be classified as land containing chemical compounds or elements at levels above those considered natural for that location. These sites cover a total area of between 100-300,000 hectares. The nature and composition of the pollutants across the contaminated sites are complex and varied, and it is probable that at every site the contamination profile will be made up of both organic and inorganic pollutants, including heavy metals [Bone et al.,2004].

In the UK, the huge expansion in the steel, coal, chemical, pharmaceutical and other industries during and since the Industrial Revolution of the 18^{th} and 19^{th} centuries, meant that production of heavy metals increased steeply and continuously for more than 100 years, leaving a legacy of land contamination [Järup, 2003], the extent of which has only recently been recognised. Lack of awareness and, disregard for the impact on the environment of uncontrolled disposal of industrial wastes, exacerbated by spillage of fuel and raw material, resulted in extensive contamination of industrial land. In addition to heavy industries, other sources of contamination included agricultural activities, atmospheric deposition, fuel distribution and laundries.

In an attempt to discourage uncontrolled waste disposal and to encourage waste recovery, the Environment Protection Act EPA (1999) introduced by the UK Government addresses remediation and re-use of brown field sites. In parallel the EU Landfill Directive [Council Directive 1999/31/EC] focused on alternative forms of disposal and recovery of industrial waste. Both were designed with sustainable waste handling, soil remediation and land re-use as key themes [European Commission,2008]. Legislation and increased awareness of the environmental damage caused by pollution have served to focus attention on contaminated land remediation, the role brown field sites are likely to play in future land use and the impact of pollutant leaching into resources such as ground water.

In order to limit or reduce further damage to the environment the techniques for the removal or stabilisation of contamination at the affected sites to prevent leaching into the environment, are the focus of much current research. The aim of this thesis is to extend the use of low cost waste materials for the stabilisation of heavy metal pollutants in metal contaminated soils and solutions.

1.2 Literature Review

The Environment Protection Act, 1990 [OPSI, 1990] defines a contaminated site as one in which there is a risk, or possible risk, of significant harm to human health as a result of substances in, on or under the land. Three key components: source, pathway and receptor must be clearly defined. Table

1.1, identifies industrial activity and the likely type of resulting contamination, and it can be seen that metals as contaminants are widespread. Table1.2 summarises derive a Soil Guideline Value (SGV) by estimating the level of a substance in soil that will result in an amount of that contaminant entering a human body that is equal to the relevant Health Criteria Values (HCV)(DEFRA 2002). in addition to metals and metalloids, lists other chemical pollutants that may be present in the soil. The health effects of exposure to heavy metals and the remedial techniques that can be used to reduce the impact of this pollution on both humans and the environment are discussed below.

Table 1.1 Industrial activities and associated pollutants. [Layla Resources, 1996]

Potential Contaminants Associated With Major Industrial Sectors		
Sector	**Contaminant**	
	Type	**Example**
Gasworks	coal tar, phenols, cyanide, sulphur	creosote, phenol, free &complex sulphide / sulphate
Iron + Steel works	metals, acids, mineral oils, coking works' residues	copper, nickel, lead, sulphuric and hydrochloric acids, (as for gasworks)
Oil refineries	hydrocarbons ,acids, alkalise, lagging, insulation, spent catalysts	various fractions, sulphuric acid, caustic soda, asbestos, lead, nickel , chromium
Petrochemical plants	acids, alkalise , metals, reactive monomers , cyanide amines, aromatic hydrocarbons	sulphuric acid, caustic soda, copper, cadmium, mercury, styrene, acrylate , VCM , toluene di-isocyanate, analine , benzene
Petrol stations	metals ,aromatic hydrocarbons, octane boosters ,mineral oil, chlorinated hydrocarbons, paint, plastic residues	barium, copper, cadmium, lead, nickel, zinc, benzene ,lead, MTBE – trichloroethylene
Textiles	metals ,acids, alkaline salts, chlorinated hydrocarbons, aromatic hydrocarbons, pesticides , dyestuff residues	aluminium, tin , titanium, zinc, sulphuric acid , caustic soda, sodium hypochlorite, trichloroethylene , phenol
Wood processing	coal tar, chlorinated hydrocarbons, metalloids/ metals	creosote , pentachlorophenol arsenic , copper, chromium
Rubber processing	metals, sulphur compounds , reactive monomers, acids,	zinc, lead, sulphur, thiocarbonate soprene,

These are the values published in the SGV series of documents by DERFA, and are based on the sandy soil described in CLR 10. They will vary according to soil type. It is very important to refer to the original source documents for full guidance on how to apply these values.

Table 1.2 Soil Guideline Values as a Function of Land Use

All values in mg/kg dry weight soil				
Pollutant	**Residential with plant uptake[A]**	**Residential without plant uptake[B]**	**Allotments[C]**	**Commercial/ industrial [D]**
Arsenic (As)	20	20	20	500
Cadmium (Cd)	1 (pH 6) 2 (pH 7) 8 (pH 8)	30	1 (pH 6) 2 (pH 7) 8 (pH 8)	1400
Chromium (Cr)	130	200	130	5000
Mercury(inorganic Hg)	8	15	8	480
Nickel (Ni)	50	75	50	5000
Lead (Pb)	450	450	450	750
Selenium (Se)	35	260	35	8000

[A] House with a garden and therefore the possibility of ingestion of home-grown vegetables

[B] House or apartment with no private garden area

[C] Open space, often made available by the local authority, for people to grow fruit and vegetables for their own consumption

[D] Assumes that work takes place in a single-storey building, factory or warehouse where employees spend most time indoors involved in office-based or light physical work. Does not apply to sites with 100% hard cover, such as car parks

The CLEA report describes the technical background to the Contaminated Land Exposure Assessment (CLEA) model. The CLEA model is used to estimate potential exposures to a substance in soil, by children and adults if they live, work and/or play on contaminated sites over long time periods. The Soil Guideline Values (SGV) set out the underlying assumptions, made to predict exposure for three standard land use scenarios (residential, allotments and commercial [DEFRA 2010]

1.2.1 Effects of Heavy Metals on Human Health

1.2.1.1 Heavy Metals

Heavy metals are usually regarded as those metallic elements with a density greater than $5x10^3kg/m^3$, and are "the most toxic inorganic pollutants which occur in soils, and can be of natural or anthropogenic origin" Bradl[2004] Metallic elements occur naturally in one form or another in all soils with a concentration that depends in the material from which the soil was formed. Environmental contamination and human exposure to heavy metals such as cadmium, mercury and lead are serious and growing problems throughout the world, and have risen dramatically in the last 50 years as a result of an exponential increase in the use of heavy metals in industrial processes and products, with many occupations involving daily heavy metal exposure. Common sources of contaminants and their effects on human health are summarised in Table 1.3. The Agency for Toxic Substances and Disease Registry (ASDR) and WHO have generally classified exposure of 14 days or less to toxic heavy metals as acute; 15-354 days as intermediate; and more than 365 days as chronic [Life Extension Foundation, 2008; USEPA, 2005].

The adverse effects of heavy metals on human health have been known for some considerable time. Toxic metals cannot be metabolized by the body and bio-accumulate (e.g. can be passed up the food chain to humans) [Robert bore et al, 2010]. The most common are arsenic, cadmium, chromium, copper, lead, mercury, nickel and zinc, but aluminium and platinum are also found. Of these, only copper, nickel and zinc have any known function in the body, and the other elements can be highly toxic. Heavy metals are usually taken into the body via inhalation, ingestion, and skin absorption Bahattin [2002]. If these enter and accumulate in body tissue faster than the body's detoxification pathways can dispose of them, a gradual build-up occurs and over time can reach toxic concentration levels. Thus, high concentration exposure is not required to produce a state of toxicity in the body tissues. Samara et al, [2009] Miretzky and Cirelli [2010] Arsenic contamination, for example, can result from metal mining and smelting, animal dips and pesticides and it is also present in wood preserving products. Arsenic is considered to be carcinogenic with cumulative poisoning occurring as result of prolonged arsenic ingestion or by the inhalation of toxic arsine gas causing respiratory cancer. Similarly, cadmium can be found in soil as a result of emissions from non-ferrous smelting

of zinc and lead in the iron and steel industry. It is also present in some fertilisers and certain sewage sludge[Zabin et al 2008].

Table 1.3 The sources of common contaminants and their health effects [USEPA, 2007]

Common source	Contaminants	Potential Health Effects
Household items, such as batteries, thermometers and paints	mercury	Toxic to kidneys
Steel and glass manufacturing	chromium, lead, mercury	All are toxics to kidney, lead causes decreased mental ability
Photocopy machines	chromium	Toxic to kidneys, potential human carcinogen
Various commercial and industrial manufacturing processes	arsenic, beryllium, cadmium, chromium, lead, mercury, PCBs	All are toxic to kidneys, decrease mental ability, weakness, headache, abdominal cramps, various skin ailments
Herbicides for vegetation control	chloropheoxy compounds, 2,4-dichloro phoenix acetic acid	Chlorines, weakness or numbness of arms and legs, long-term nerve damage
Pesticides	chlorinated ethane's, DDT, lindane	Acute symptoms of apprehension, irritability, dizziness, disturbed equilibrium, tremors and convulsions, kidney damage.
Electrical transformers and other industrial machinery	polychlorinated biphenyls (PCBs).	Various skin ailments including chloracne, may cause liver toxicity, carcinogenic to animals
Commercial solvents	benzene, toluene, xylene.	Benzene suppresses bone marrow function, causing blood changes, chronic exposure can cause leukemia
Chemical manufacturing	benzene, ethyl benzene, toluene.	Central nervous system, depression, dermatitis
Dry cleaning agents and degreasers	trichloromethane and tri - chlorso ethylene.	Central nervous system
Car radiators and de-icing agents	ethylene glycol	Can cause abdominal pain, vomiting, weakness, dizziness, damages central nervous system, depression

Acute toxicity is usually from a sudden or unexpected exposure to a high level of the heavy metal (e.g., from careless handling, inadequate safety precautions, or an accidental spill or release of toxic material often in a laboratory, industrial, or transportation setting). Chronic toxicity generally results from repeated or continuous exposure, leading to an accumulation of the toxic substance in the body, and may result from contaminated food, air, water, or dust; living near a hazardous waste site; spending time in areas with deteriorating lead paint; maternal transfer in the womb; or from participating in hobbies that use lead paint or solder. Chronic exposure may occur in either the home or workplace. Symptoms of chronic toxicity are often similar to many common conditions and may not be readily recognized. Routes of exposure include inhalation, skin or eye contact and ingestion.

1.2.1.2 Human Exposure

Heavy metals may enter the human body through food, water, air, or absorption through the skin. Human exposure could be through their use in agriculture and in manufacturing, pharmaceutical, industrial, or residential settings. Industrial exposure is a common route of exposure for adults while ingestion is the most common route of exposure in children [Roberts, 1999]. Assessment of human exposures to any heavy metal (or chemical agent) includes (1) identifying how people came into contact with the metal in the environment; (2) determining the concentrations of specific forms (speciation) of the metal in specific media (e.g., soil, water, air, and biota); (3) identifying the pertinent exposure routes (via a dose-response assessment); (4) estimating the exposure route (e.g. oral intake, inhalation exposure concentration, blood concentration), which may involve quantifying relationships between exposure concentrations and intakes; and (5) identifying sources of uncertainty and natural variability and, where possible, quantifying these in the estimates of exposure. [Peakall and Burger 2003] .

In the developed world, legislation and social awareness has meant, for example, a dramatic decrease in the use of arsenic as a common wood preservative, or lead tetraethyl as a common additive to petrol. However, exposure to heavy metals is increasing for many people, for example, in many parts of the developing world (especially Latin America), mercury is still widely used in gold mining. Figure 1.1 shows the global production rates of certain toxic metals for the period between 1850 and 1990. Note the emission of heavy metals has started to decrease in developed countries according to Järup [2003], who cited the DETR Report of 2001 that there has been a drop in the emission of heavy metals in UK between 1990 and 2000 of about 50%.

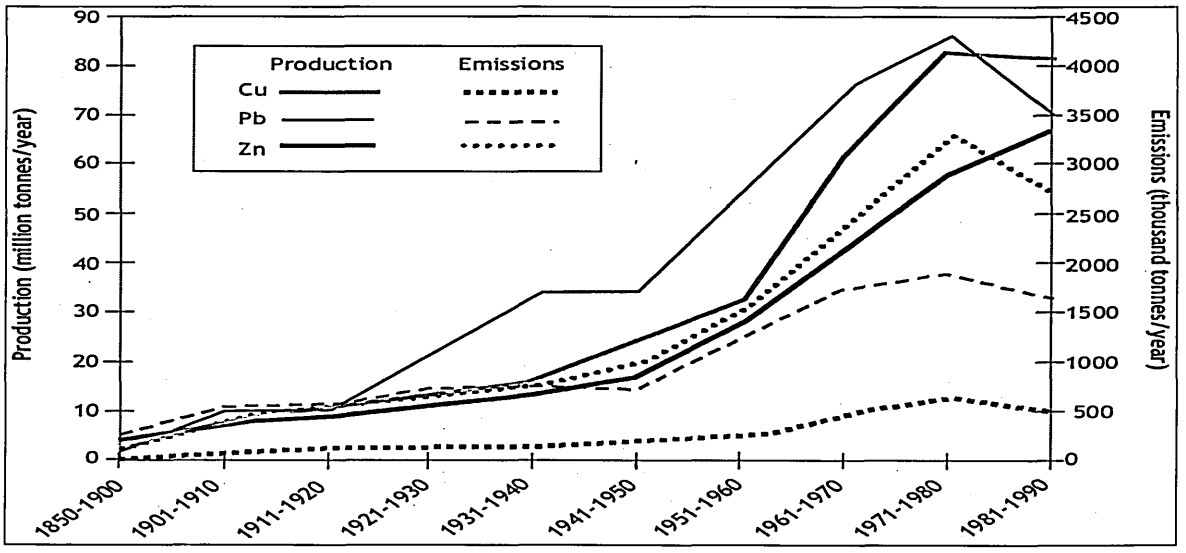

Figure 1.1. Global production and consumption of selected toxic metals (Copper, Lead and Zinc), 1850-1990 from Järup [2003]

In the USA the fuel and power industries generate about 2.4 million tonnes of heavy metal waste annually. Agriculture and waste disposal add about another 2 million tonnes. These contribute substantially to the contamination of soil and groundwater by heavy metals which are prevalent at waste sites across the United States [Prabhukumar et al 2005].

1.2.1.3 Impact of Heavy Metals on Human Health

Heavy metals become toxic when they are not metabolized by the body and accumulate in the soft tissues [Life Extension Foundation, 2008]. As a rule, acute poisoning is more likely to result from inhalation or skin contact of dust, fumes or vapours, or materials in the workplace. However, lesser levels of contamination still occur in residential settings, particularly in older homes with lead paint or old plumbing [International Occupational Safety and Health Information Centre, 1999]. However, metals are associated with numerous health effects that have been reviewed in detail in reports issued by the WHO's International Programme 5 [WHO, 1975], which categorises at least arsenic, beryllium, cadmium, chromium (VI), and nickel as known human carcinogens in one form or another, or in particular routes of exposure. Inorganic lead compounds are also considered probable human carcinogens. Other effects of metals are also well documented, including effects on the cardiovascular, epidermal, gastrointestinal, haematological, immunological, musculo-skeletal, and neurological systems [USEPA, 2005]. The US EPA considers lead, cadmium, arsenic, copper, zinc, mercury and nickel, as the most hazardous elements in the priority pollutant list [Mulligan and Yong 2001]. The US EPS strongly recommend that all necessary action is taken to remediate these

elements before they enter the general environment and adversely affect human health [USEPA, 2005].

Britain has a long history of industrial production and throughout the UK there are between 50,000-100,000 sites, occupying at least 100,000 hectares, where land has become contaminated by human activities such as mining, industry, chemical and oil spills and waste disposal [DEFR, 2000 ; Bone et al., 2004]. Contamination can also occur naturally as result of the geology of the area, or through agricultural use.

Over the past decades there has been a boom in housing prices and a growth in the number of households, combined with greater environmental awareness and the protection of greenbelt and agricultural land. Indeed government perspectives envisage the construction of more than 2 million new homes by 2016. Of these 60% are expected to be on brown field sites (Urban Environment Agency. 1998). This has introduced great commercial and social pressure for the rapid re-development of land previously used as industrial sites. Unfortunately, this previous usage has often left unsafe levels of pollution which, if untreated, would mean no dwellings could be built on the sites [Al-Tabbaa and Perera 2005]. Stabilisation/solidification (S/S) is a technique acceptable within the UK Government's strategy for the remediation of contaminated land, [see Part IIA of the EPA 1990a].

1.2.2 Remediation Techniques

1.2.2.1 The Need for Remediation

Remediation may be required for the treatment of contaminated soil, contaminated debris, contaminated groundwater, and even the source of the contamination. Its primary aims are to reduce the actual or potential environmental threat and reduce potential risks to acceptable levels.
Consequently, the need for any remediation will depend on the degree of any actual or potential environmental threat or the level of any risk. Aspects of risk will, in turn, depend partly on the expected end-use of the site following remediation, as different at-risk targets can be associated with different end-uses, so remedial treatment criteria are based on the site's final usage.[DEFRA.2008] for example the need of land to re-build on reconstruction of contaminated land ,the stabilization and solidification technology it would be the most desirable approach.

1.2.2.2 Remediation Methods

The general modelling approach of source, target and interconnecting pathways is used to assess the risk of the contaminated sites and selection of remediation methods. Groundwater monitoring then provides an indication of the integrity of the sites' remediation. Cost benefit analysis in conjunction with an examination of the extent and types of pollution present, as well as the groundwater regime permits an extensive evaluation of remediation techniques to be used. Assuming that a remedial approach can be adequately monitored and controlled, there is an increasing desire to promote on-site solutions [Crumbling and Lesnik 2001; CLARINET 2002].

Civil engineering techniques are the most widely applied remediation technologies throughout Europe [Arctander and Bardos, 2002]. These include: excavation and related materials handling and disposal of contaminated soil, infilling the void and covering systems using vertical barriers. Another important group of remediation technologies are those which prevent the development of hazardous gases in the ground, and include:

a) soil, vapour extraction / bio-venting,
b) air / biosparging, soil flushing, pump and treat, permeable reactive barriers,
c) redox amendments for bioremediation oxidation, and
d) electro-remediation, phytoremediation, monitored natural attenuation.

The predominant technologies that are used for the treatment of soils include: bioremediation, soil washing and related techniques such as solidification and stabilisation, and thermal treatments. Table 1.4 summarises the techniques commonly used for soil remediation.

Table 1.5 summarises the main i*n-situ* and *ex-situ* remediation techniques (sub-divided into physical, chemical, biological and thermal) and their suitability. The technical options for managing contaminated land and contaminated water (both non-radioactive and radioactive) can be grouped into three main categories [Mallett 2004]:

1. Partial or complete removal or destruction of the contamination,
2. Immobilisation or stabilisation of the contamination, and
3. Isolation and containment of the contaminated soil.

Table 1.4. The Current techniques used for remediation of contaminated land [from Wood, 1997]

Removal of contaminated soil (the 'Target') to landfill		
Contaminated waste		
Hazardous waste, e.g. heavy metals, polymers		
Special waste, e.g. nuclear waste		
Containment of contaminants (the 'Source')		
Encapsulation, slurry walls, jet grouting, blankets, clay, plastic membrane, vitrification, cementation and capping		
Removal of contaminant (the 'Source')		
Physical	**Chemical**	**Biological**
Soil wash	Ion exchange	Anaerobic bacteria
Drum removal	Neutralisation	Fungi
Evaporation	Oxidation	Land farming, composting
Steam stripping	Photolysis	Phytoremediation
Vacuum air stripping	Precipitation	
	Carbon adsorption	
	Reduction	

Table 1.5. Summary of remediation techniques and their applicability [Bone et al 2004]

Category	In-site technique	H.M.	Organic	Radio-logical	Ex-site	H.M.	Organic	Radio-logical
Physical	Electro remediation	M	M	E/M	Excavation and disposal	C	C	C
	Capping	C	C	M	Soil washing	C	C	E
	Barrier	C	C	M	Electro remediation	E	E	M
	Hydraulic containment	M	M	M	Soil vapour extraction	N/A	C	N/A
	Detector based segregation	N/A	N/A	C				
	Soil vapour/ dual phase extraction	C	N/A	N/A				
Chemical	Soil flushing by chemical leaching	C	C	M	Soil washing by chemical treatment	C	C	E
	Solidification / stabilisation	C	C	C	Chemical treatment	C	C	E/M
	Surface amendment	M	M	M	Solidification / stabilisation	C	C	E/M
					Surface amendement	M	M	M
Biological	Phytoremediation	E	E	E/M	Bioremediation	N/A	C	N/A
	Monitored natural attenuation	C	C	M				
	Bioremediation	N/A	C	N/A				
Thermal	Vitrification	M	M	M	Incineration/ thermal	C	C	N/A
					Adsorption, vitrification	M	M	E

Key: C Commonly used, well developed technology, effective, **M** Maybe suitable either in conjunction with other techniques, and/or following detailed consideration of site-specific characteristics. **E**; Experimental/ pilot scale; **N/A,** Not Applicable, **H.M**; heavy metals.

1.2.2.2.1 Solidification/Stabilisation (S/S)

Stabilisation is a process whereby a toxic waste is converted to a form that is physically and/or chemically more stable. The hazardous waste has its form changed to one that is less mobile or less toxic, which may include chemical interaction between the waste and a binding agent. On the other hand, solidification is used to convert liquid or semi-solid waste (including powders) into a form (such as a granular material) that will allow relatively easy and safe handling and transportation to landfill sites [Conner, 1990; Glasser, 1997; Poon et al., 2004, Chen et al., 2009].

S/S uses known civil engineering techniques, whereby the contaminated soil is mixed with a binder that improves its engineering properties and simultaneously fixes the contaminants. S/S has a proven record of successfully treating a broad range of contaminants, and is commonly used to remediate metal, radioactive,.etc. contaminated soil [Rossetti and Medici 1995; Conner and Hoeffner, 1998a; Malviya and Chaudhary, 2006]. For the past fifty years S/S has been extensively used as a remediation treatment in the USA, however in the UK, and a number of other countries, S/S is a technology which has yet to be implemented [Malviya and Chaudhary, 2006; Chen et al. 2009]. This is partly because of the availability of alternative cheaper options such as landfill but, increasingly, government policies and national and international legislation are making such options less sustainable, and less commercially attractive.

Lime is widely used in S/S for stabilising soils and improving their engineering properties [Bujang et al, 2005]. Extensive experience gained in the EPA, USA has been reviewed and published advice is widely available. http://www.epa.gov/tio/tsp/download/542f06013.pdf. Nevertheless, it remains a fact that S/S projects are more challenging to implement than traditional soil stabilisation techniques in terms of the strength of products, and it is often the case that consulting engineers, contractors and environmental enforcement officers lack the necessary knowledge about it. To encourage the wider use of S/S in the UK, the British Cement Association, the British Lime Association and the UK Environment Agency co-operated to develop simple, robust guidance for the design and step by step implementation. [www.environment-agency.gov.uk]. The guidelines were produced for the UK, but the principles are applicable to all countries.

As recently as 2004, an assessment of household, commercial and industrial waste disposal in the UK [Bertos et al., 2004] revealed that over 75% of the waste produced in London and the Thames Region (22 million tonnes per year) ended up as landfill. However, the legal restrictions on disposal to landfill means that landfill sites for the South East of England cannot be increased beyond the area in use in 2005. This is a major factor driving the growing interest in S/S and the re-cycling of specific waste materials, including the products of incineration or composting.

S/S is a remediation technique that requires the addition and mixing of controlled amounts of hydraulic binders with the contaminated soil to form a new solid, which can range in form from granular to a solid block within which the contaminants are rendered immobile and virtually non-leachable [Bromag,2004]. Although not removed, the contaminants are prevented from being able to cause harm.

Stabilisation occurs when certain reagents are added to chemically modify the contaminants to produce stable constituents. This will involve a number of processes such as adsorption, precipitation of more soluble forms and the formation of low-solubility salts, for example, precipitation of heavy metals as insoluble hydroxides. Solidification requires the addition of other the contaminants within a solid product, making it more stable and less prone to being affected by external agents such as percolating groundwater that may transport the contaminants through agents to produce a physical alteration of the soil, creating a dimensional stability containing the soil [Raj et al.2005; Paria and Pak K. Yuet.2006].

Depending on the contaminant, the type of soil and the reagents added, a wide range of immobilisation mechanisms are possible, including physical containment of the contaminant or chemical reactions between the reagent and contaminant to change the nature and/or mobility of the latter such as adding and mixing the cement to contaminated soils, however . The most common binders used in the UK are: lime, cement, fly-ash, ground-granulated blast furnace slag (GGBFs) and pulverised-fuel ash (PFA). These may be used either separately or in combination in order to immobilize the pollutants. [Bone et al., 2004]Additional small quantities of additives or admixtures may be included in the binder to enhance performance and fine-tune the efficiency of the treatment. S/S of hazardous wastes by pozzolan-based binders is a now familiar technology that has been applied to many types of industrial wastes containing heavy metals to minimize the threat

to the environment, and ensure compliance with existing regulatory standards [Srivastava et al, 2008]. Pozzolanic materials harden with water but only after activation with an alkaline substance such as lime. Such additives may be purchased 'off the shelf' as proprietary products or as more generic reagents. The list of possible additives is extensive and includes: wetting agents, sorbents, pH/redox modifiers and flocculants [Conner and Hoeffner 1998; Shi and Spence 2004].

The binders cement, lime, GGBFA, PFA and fly ash) and additives (pH/Redox modifiers; wetting agents; flocculants and sorbents) may be added to the soil using a variety of methods which include: modified excavation plant, rotovator-type plant, augurs and sub-surface injection; or a so-called 'treatment train' that involves a range of treatment processes. The exact mixing approach is determined by the types of soil and contaminant, and the depth at which the contamination occurs. Despite the nature of the soil, contamination, and remediation goals being different for each and every project, the versatility of S/S means that the technique is fully able to deliver a customised solution for each remediation project [Bromag 2004].

Solidification technologies are not limited to the addition of chemical agents to contaminated soil to form a mixture that sets as a firm mass with enhanced structural integrity and reduced permeability. They also include the use of high temperatures where the soil is heated by electricity and a glass-forming additive is mixed with the soil. This vitrification process is carried out on site, producing a molten glass product, which is subsequently removed. [Raj et al 2005]

Stabilisation technologies may also use chemical agents to react with soil contaminants to convert them into less toxic and/or mobile forms. For example adding binder agents as Portland cement, cement kiln dust (CKD), lime, lime kiln dust (LKD), limestone, fly ash, slag, gypsum and phosphate mixtures. Stabilisation does not necessarily result in solidification, although both techniques are commonly used in tandem. Solidification and stabilisation treatments require the addition of amendments, for example pozzolans such as cements, lime and incinerator ash, to cause the solidification, as well as binders and agents to facilitate setting. Pozzolan based systems can be applied using conventional mixing approaches, for example via a hollow stem auger. Technologies aimed at the stabilisation of organic compounds include amendments such as organophilic clays or activated carbon.

Alternatives to pozzolan-based systems include the use of asphalt. [Contaminated Land Rehabilitation Network .2002]

With S/S technologies, there are problems assessing the long-term performance and, at present, the absence of an agreed protocol for prediction of long term weathering of the stabilised product results in the inability to test the predicted long-term effect of the process, and so limits the possibilities for regulators to approve the technology [Contaminated Land Rehabilitation Network, 2002].

Because of the effectiveness of cement-based S/S processes for treating radioactive waste, their use has been extended to the treatment of industrial waste liquids, sludges and filter cakes. S/S technology has long been used at landfill sites to achieve the "no free liquids" requirement of the 1976 Resource Conservation and Recovery Act and the 1984 Hazardous and Soils Wastes Amendments Act. [Cullinane and Jones, 1989]. A number of companies offer treatment of hazardous wastes and many S/S processes have been developed and registered by these companies, including processes using combinations of reagents such as Portland cement and sodium silicate Conner [1990].

S/S processes have also been developed to treat industrial sludges containing inorganic and a range of other difficult industrial wastes. In the UK there are currently only a very small number of commercial S/S processes available for hazardous waste. This is primarily because UK waste management licensing policies continue to permit co-disposal of heavy metal containing wastes, which would be most suited to S/S treatment. It is estimated that about 70% of hazardous wastes produced in this country is sent to licensed co-disposal landfills and this has severely limited the development of commercial S/S processes [Holmes1996], [Hester and Harrison 1997].Despite S/S being an established technology for treatment of hazardous waste and remediation of contaminated soils in a number of EU member states and the USA, uptake in the UK has been poor. Bone et al [2004] have identified barriers to the acceptance of S/S. These include: liability resulting from immobilised contaminants remaining on-site (see Corby City Council's out-of-court settlement in April 2010 of personal injury claims arising from mistakes made in the cleanup of contaminated land at the former British Steel site [www.workplacelaw.net/news/display/id/27427];there is uncertainty concerning the durability and rate of contaminant release from S/S-treated material; The UK lacks authoritative technical guidance on S/S; and experience of past poor practice during the

1980s and 1990s in the application of cement stabilisation processes to waste disposal [CLAIRE Guidance, 2005] .

Nevertheless, in Italy, Scanferla et al. [2009] have successfully used S/S to reduce the leaching of heavy metal from contaminated soils. Pensaert et al [2008] have used innovative S/S techniques in two important field cases.The first was in the UK and concerned the 2012 London Olympics site; the second was the treatment of land in Belgium contaminated by tar oil. Pensaert et al [2008] concluded that successful immobilisation of contaminated soils can be achieved using a mix that does not contain cement. While not new in theory, Pensaert et al [2008] recommend this innovation not only as a valuable alternative to the classic treatments for soils, but as an additional solution for soils that cannot be treated by conventional techniques (see Section 1.2.2.2) and are presently being sent to landfill for disposal.

In the UK, there is increasing interest in the application of S/S technology, and it is expected that the implementation of the draft landfill directive could significantly change the status and level of application of solidification technology is in the UK. According to Pensaert et al, [2008], S/S technology was first developed as a treatment for hazardous waste that would then be used for land fill, but that over the last twenty or so years it has also been applied as remediation for contaminated soils for a variety of contaminants including heavy metals, with most reported cases being solidification by means of hydraulic binders such as cement [Wilk 2009].

Contaminated land reclamation

The perceived benefits of S/S have resulted in its being used increasingly to reclaim contaminated land. In the USA, S/S is used for about a quarter of all remediation carried out under the Comprehensive Environmental Response Compensation and Liability Act (CERCLA), to resolve difficult situations where hazardous substances pose a potential danger to human health and the environment.

Currently, cementitious solidification is the "best demonstrated available technology (BDAT)" for land disposal of toxic elements, according to the US Environmental Protection Agency (USEPA 1999). Alkaline matrices such as calcium hydroxide and cement are commonly used in waste conditioning because they are inexpensive, readily

incorporate wet wastes and their alkalinity reduces the solubility of many inorganic toxic or hazardous metals [Singh and Pant 2006].

Sustainability

Brownfield sites in the UK often have complex contamination profiles and physically challenging conditions. Soil stabilisation is well suited to the redevelopment of such sites as it allows the on-site recycling of materials, thus meeting the objectives of sustainability while being compatible with UK and EU legislation. Importantly, it offers a cost-effective alternative to landfill, an advantage that should encourage its greater use in the UK. The EU Landfill Directive 1999, implemented in the UK as the Landfill (England and Wales) Regulations 2002, and Landfill (Scotland) Directive 2002, calls for a profound change in current landfill practice. The UK Environment Agency supports the use of processed-based technologies, such as S/S, as a best practice technique and views it as an important method for the pre-treatment of wastes prior to disposal. Pre-treatment of landfill wastes is necessary under EU directives and subsequent UK regulations. [DEFRA2000]

1.2.2.2.1.1 Stabilisation/Solidification Mechanisms

The goal of S/S is to achieve and maintain certain required physical properties, and to chemically stabilise and/or permanently bind the contaminants.

A - Physical mechanisms

Solidification is the technique of encapsulating the waste within a single (sometimes uniform) solid coating of high structural integrity, and does not require chemical interaction between the waste(s) and the solidifying agent(s), but can be achieved by mechanically binding the waste into the monolith [Conner and Hoeffner, 1998a]. The physical mechanisms involve confining of waste constituents within a low permeability matrix, which isolates the waste from environmental influences. In the S/S process encapsulation occurs at both the micro and macro-scale [Lubowitz and Wiles, 1979]. Micro-encapsulation is the process whereby waste is trapped or adsorbed within the solidified matrix. The contaminants do not necessarily interact chemically with the solidification reagents. Macro-encapsulation is used to describe the process in which a solid or cemented waste form is coated with, or contained in, an impermeable layer. It may

also refer to the containment of large waste solids in drums or containers [Marty et al.1985].

By isolating the waste(s) within an impervious capsule, solidification substantially decreases the surface area of the waste which is exposed to leaching and so restricts and/or eliminates contaminant migration.

B- Chemical mechanisms

A number of chemical mechanisms are included in S/S processes:
pH control: pH plays an important role in controlling the solubilities of heavy metals, this is because most heavy metals are amphoteric for instance Pb, Ni, Cd, etc which means that their solubility increases at higher or lower pHs above their minimum solubility. The minimum solubility of most metal hydroxides occurs within the approximate pH range of 7.5-11. In S/S processes, lime can be used to control pH. Other alkali-solidifying reagents such as Portland cement can be substituted for lime [Wilk 2009].

Precipitation: Hydroxide precipitation is the most common immobilisation mechanism in the S/S process. In cases where waste for S/S treatment contains a number of different metals with very different minimum solubility pH values, it is difficult to choose the pH value that is optimum for precipitation of all metals. Under these circumstances it may be necessary to precipitate the metals as carbonates, phosphates, silicates and sulphides, rather than hydroxides [Means et al.1995].In this study according to XRD analysis the precipitation of metals were mostly as carbonate, silicate and sulphides.

In soils, the sorption of metals is directly and indirectly affected by pH. The pH-dependent sorption reactions of cationic metals are partly due to the preferential sorption of hydrolyzed metal species in comparison with the free metal ion The proportion of hydrolyzed metal species increases with pH. Additionally, adsorption sites in soils and sediments are pH-dependent, the number of negative sites for cation sorption decreasing with decreasing pH. Moreover, under alkaline conditions, trace metals can precipitate as oxides, hydroxides, carbonates and phosphates [Cappuyns et al.2008]. Dijkstra..et al [2006] reported of precipitation of that's explain solubility of Pb as function of pH $PbCO_3$ (although not shown) or Hydrocerrusite ($Pb_3(CO_3)_2(OH)_2$

Metals and precipitation

Both Cory [1981], Cocke [1990] and Li et al [2002] have discussed adsorption vs. precipitation and summarised the processes as follows:

1. Crystal growth occurs if the adsorbate is a component of the cement adsorbent. Such as adsorption of heavy metals on the surface of fly ash and precipitation.
2. Crystal growth and/or diffusion into the solid phase occurs if the adsorbent is not a component of the adsorbent but can form a solid solution.
3. Stabilisation of metal poly-nuclear ions occurs by adsorption onto a positively charged surface of the adsorbent.
4. Hetrogeneous nucleation of a new solid phase may involve a new phase composed of the adsorbate and a component from the solution (hydroxides, carbonates etc).

1.2.2.2.1.2 Classification of S/S Processes

S/S processes are generally classified based on the type of solidifying reagents used and on the waste being treated. They are grouped into organic and inorganic processes. Organic S/S processes have narrower applications than inorganic processes and are used only for specific types of wastes and therefore these types of processes are only briefly discussed.

1.2.2.2.1.3 Organic Processes

The basic S/S processes use either thermoplastic or thermosetting organic polymers. A thermoplastic process involves the dispersing of dried wastes through the heated plastic, which when cooled, will incorporate the wastes into a rigid but deformable solid [Schnoor, 1997]. A thermosetting process involve the use of a monomer that is polymerised or cross-linked by the use of catalysts or accelerators after being mixed with liquid waste [Mahalingam et al.,1981]; Panda et al., 2010]. There is usually no direct reaction between the waste constituent and the polymer. Urea formaldehyde is the most common organic polymer currently in use. However, due to high operational costs and skilled labour requirements, its use has been limited to primarily nuclear waste application. The geopolymers system is similar to cement in terms of encapsulation, but it does have improved chemical and physical properties such as durability and structural integrity, low permeability and high compressive strength. Galiano et al [2010] and Coz et al[2009] used S/S technology to treat organic matter from gas plants, and reported using foundry sand

ash as an additive. They concluded that foundry sand ash can be used as a replacement for cement products but that the best results were obtained using mixtures of cement and sodium silicate as binding material. A silicate content range of 5–25% (in the mixture with cement) are optimum leachability for organic matter.

However, the use of S/S is now required in since many contaminated sites still exist. a survey by the American Petroleum Institute (API) revealed that 6×10^9 Lpa of drill cuttings are generated in the USA. Between 50,000 and 80,000 Lpa of drill cuttings have also been reported to arise in the UK [UKOOA 2002]. The contaminants present in drill cuttings depend on the chemistry of the drilling mud used and the composition of the formation rock. These contaminants include petroleum hydrocarbons, such as aliphatic hydrocarbons and polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and heavy metals including barium, lead, zinc, mercury, chromium, arsenic and nickel [UKOOA 2002] [Leonard and Stegemann, 2010].

1.2.2.2.1.4 Inorganic Processes

Inorganic processes are normally used to solidify water-based wastes, sludges, and filter cakes. These processes are based on hydraulic reactions of the hydraulic cements or pozzolanic reactions between Portland cement or lime and pozzolanic materials. The most common inorganic reagents used in the S/S process include: a) Portland cement /lime, b) Portland cement /lime /fly-ash, c) Portland cement /lime /fly-ash /kiln dust, and d) Portland cement /sodium silica [Means et al. 1995].

The major advantages and disadvantages of S/S processes are given in Table 1.6 and recent commercial applications of S/S are presented in Table 1.7 below.

1.2.2.2.2 Chemical Remediation

Chemical treatment processes for the remediation of contaminated soil are designed either to destroy contaminants or to convert them into less environmentally hazardous forms. Chemical reagents are added to the soil to bring about the appropriate reaction. Often, excess reagents may need to be added to ensure that the treatment is complete. This in turn may result in excessive quantities of un-reacted reagents remaining in the soil following treatment. Heat and mixing may also be necessary to support the chemical reaction. Chemical processes can also concentrate contaminants in a manner similar to physical

processes. A range of chemical remediation processes are at various stages of development, both for *in situ* and *ex situ* applications. Many of these are based on the treatment of waste water or other hazardous waste. However, the range of processes that have been widely used at full scale is restricted, but includes: de-chlorination, extraction, hydrolysis, oxidation - reduction and pH adjustment. [Goi.et al 2006]

An oxidation - reduction (redox) reaction is a chemical reaction in which electrons are transferred completely from one chemical species to another. The chemical that loses electrons is oxidised while the one that gains electrons is reduced. Redox reactions can be applied to soil remediation to achieve a reduction of toxicity or a reduction in solubility. Oxidation and reduction processes can treat a range of contaminants including organic compounds and heavy metals. Oxidising agents that can be used include chlorine gas, hydrogen peroxide, oxygen, ozone, ozone and ultraviolet light and various chlorine compounds.

Table 1.6 Advantages and disadvantages of solidification/stabilisation [CIRIA, 1995]

Advantages	Disadvantages
Applicable to inorganic and organic contaminants, although organics are less proven. Applicable to soils, sludges and liquids Improved geotechnical properties Rapid treatment possible *Ex situ* methods relatively easy to apply	Contaminants contained rather than destroyed or detoxified Increase in volume of material following treatment Some processes produce heat which can cause gaseous emissions Quality assurance measures needed, especially for *in situ* methods Uncertainties over long-term performance, especially with organic contaminants Long-term monitoring required

Table 1.7 Modified recent commercial applications of solidification/stabilisation treatment of wastes in the UK [Al-Tabbaa and Perera, 2002]

Waste	Process	End Use	Reference
Lightly contaminated silt	PFA and lime	Lightweight embankment fill	Al-Tabbaa and Perera, 2002a
Heavy metals, PAHs, cyanides, etc.	Cement	S/S. London Olympics 2012 Site	Pensaert. et al 2008
Intermediate level radioactive waste (ILW) and low level radioactive waste (LLW)	PC and blast furnace slag or PFA	Stored in designated repository	Al-Tabbaa and Perera, 2002b
Mercury contaminated dredging	PC and PFA blend	Disposed of to landfill	Guha, 2002
(Pit wines) former gas works site	PC and slurry	Re-use the site	Williams, 2007

Reducing agents that can be used include the metals aluminium, sodium and zinc, as well as alkaline polyethylene glycols and some specific iron compounds [Mallett, 2004]. For example, compounds containing highly oxidized chromium are toxic whereas their reduced counterparts are much less dangerous [Ibanez, 2004].

Chemical de-chlorination processes use reducing reagents to remove chlorine atoms from hazardous chlorinated molecules to leave less hazardous compounds. De-chlorination can be used to treat soils and waste contaminated with volatile halogenated hydrocarbons, polychlorinated biphenyls and organo-chlorine pesticides. Extraction techniques that can be used for the treatment of contaminated soil include organic solvent extraction, supercritical extraction and metal extraction using acids. The methods are applicable to soils, waste, sludges and liquids. Following extraction of the contaminant the extracted liquid containing the contaminant has to be collected for treatment [Sahuquillo et al., 2003].

Hydrolysis refers to the displacement of a functional group on an organic molecule with a hydroxide group derived from water. A restricted range of organic contaminants is potentially treatable by hydrolysis, although hydrolysis products may be as hazardous, or even more hazardous, than the original contaminant. Adjustment of pH refers to the application of weakly acidic or basic materials to the soil or groundwater to adjust the pH

to acceptable levels. A common example is the addition of lime to neutralise acidic agricultural soils. Neutralisation can also be used to affect the mobility or availability of contaminants such as metals by enhancing their precipitation as hydroxides [Lin and Lin, 2005]. Chemical S/S can be applied to many contaminants, including all classes of radioactive waste, organics, inorganic, heavy metals, and mixed waste. These processes may not be effective on some organics (e.g., semi-volatile organic compounds and pesticides) that can inhibit the chemical bonding of stabilizers or the mechanical bonding of solidifying agents. [CPEO 2002].

Chemical stabilisation uses chemical reactions to transform mobile heavy metals into low toxic and hardly dissolvable forms. Thiourea, sodium hydroxide, sodium sulphide and EDTA (ethylenediamine tetraacetic acid) are commonly used chemical agents. However, Yan-Hui [2002] has demonstrated that sodium hydroxide is not suitable for lead stabilisation, though the other three chemicals are. However, sodium sulphide is not chemically stable and both thiourea and EDTA are very expensive. Thus, Zhang et al., [2007] have concluded that chemical stabilisation is not always a desirable disposal approach. Because chemical S/S processes require that potentially large volumes of bulk reagents and additives be transported to project sites, it may not affect volume or toxicity [CPEO 2002].

1.2.2.2.2.1 Limitations of Chemical Remediation

Although chemical S/S may effectively reduce the mobility of contaminants, it may not affect volume or toxicity. This approach usually requires capping or covering, engineering controls, and/or institutional controls. If the solidified material contains radioactive contaminants, a soil cover sufficiently thick to absorb gamma radiation is required. Chemical S/S processes require that potentially large volumes of bulk reagents and additives be transported to project sites. The future use of the site may also 'weather' the materials and affect the ability to keep contaminants stabilized. In addition, some processes result in a significant volume increase up, to double the original [CPEO, 2002]. A summary of the major advantage and disadvantage of chemical based remediation techniques is given in Table 1.8.

Table.1.8 Summary of the major advantages and disadvantages of S/S chemical processes

Advantages	Disadvantages
Applicable to wide range of matrix types if good mixing/contact is achieved High degree of chemical specificity possible	Effectiveness requires good mixing/contact which may be difficult with some soils Un-reacted chemical reagents may remain in the soil Any intermediate or by-products may be hazardous Pre-processing may be needed to remove debris, for size reduction or to form slurry Effective environmental control of *in situ* methods difficult

1.2.2.2.3. Physical Processes of remediation

Physical processes separate contaminants from uncontaminated material by exploiting differences in their physical properties (e.g. density, particle size, and volatility), by applying external forces such as abrasion, or by utilising differences in physical characteristic to enable separation to occur (e.g. flotation). Depending on the nature and distribution of the contamination within the soil, physical processes may result in the segregation of differentially contaminated fractions (for example a relatively uncontaminated material and a contaminant concentrate based on a size separation) or separation of the contaminants (for example oil or metal particles) from the soil particles. Table 1.9 summarises the main advantages and disadvantages of physical processes. The physical processes available include a variety of methods that are based on both *in situ* and *ex situ* approaches. This variation has been classified into two main groups, washing/sorting and extraction treatments. [Scullion ,2006] [Khan et al 2004].

Table .1.9 Advantages and disadvantages of physical processes

Advantages	Disadvantages
Some methods are already, or are becoming, established protocols Potential to reduce volume of material requiring disposal or expensive treatment Wide range of contaminants treatable Wide range of materials treatable Some *in situ* methods require only little site disruption Mobile plant available for some methods	Secondary waste streams may require treatment or disposal Soils with high clay or peat content may be difficult to treat Use of some solvents will have health and safety implications Quality assurance measures needed, especially for *in situ* methods Approval by regulatory authority may be needed

1.2.2.2.3.1 Washing and Sorting Treatment

Washing and sorting treatments are commonly referred to as soil separation and washing. The main aim of the processes is to concentrate the contaminants into a relatively small volume so that the costs associated with disposal and further treatments are related only to the reduced volume of processed residues. Washing and sorting falls into two main categories:

Separation from the soil of those particles containing the contaminants by mineral processing techniques, exploiting differences in the properties of individual soil particles. The volume of contaminated material requiring further treatment or disposal is thereby reduced [Bhandari. et al 2000,Khan et al 2004].

Removal of contamination from particle surfaces by scrubbing or attrition processes, or its transfer into an aqueous phase by leaching using liquid extractants or steam. The contaminant rich leach liquor can then be treated as waste water. Washing and sorting treatments have been used in several countries, particularly Germany and the Netherlands, for the treatment of a range of soils and contaminants. Their use in the United Kingdom is restricted although they have been used on occasion.

Extraction treatments involve processes that remove the contaminants from soils by use of a mobilising and/or releasing process to remove the contaminant from the soil matrix. Three main categories of extraction treatments are:

Soil vapour extraction an *in-situ* process where a vacuum is applied through extraction wells to create a pressure gradient that induces gas-phase volatile contaminants to flow through the soil to the extraction wells where they then are removed from the soil [USEPA, 2001].

Electro-remediation is an *in-situ* process where an electrical current is passed through an array of electrodes that are embedded in the soil. When the current is applied, movement of contaminants in the pore water towards the electrodes is induced by electrolysis, electro-osmosis and electrophoresis. The electrodes have porous housings into which purging solutions are pumped to remove the contaminants and bring them to the surface. The purging solutions are then pumped to a water treatment plant for contaminant removal.

Soil flushing and chemical extraction, which are processes that use chemical reagents, solutions or steam to mobilise and extract contaminants from soils. Mobilisation refers to the release of dissolved contaminant ions from sorbed or precipitated forms in soils and may form part of both *in situ* soil flushing or *ex situ* chemical extraction treatment.

1.2.2.2.4 Thermal Treatments

This approach uses elevated temperatures to remove and destroy or to immobilise contaminants in soil particles through physical processes such as volatilisation, combustion, and pyrolysis. Thermal systems are most commonly used to treat soils contaminated with toxic organic compounds, which are then destroyed at high temperatures. Thermal treatments can also be used to remediate soils contaminated with asbestos (decomposition of blue asbestos takes place at about 900^0C). Volatile heavy metals, such as mercury, may also be removed from soils by thermal processes, although they are not destroyed and have to be recovered downstream of the process. Established thermal treatments are uncommon; however, a number of systems are being developed.

Thermal treatments are often described as either one stage destruction or two stage destruction processes. However, it is difficult to distinguish between the two processes, for example a one-stage process is where organic contaminants are combusted within the soil matrix by heating the soil to high temperatures. However, such systems often include a secondary chamber to treat volatilised contaminants in the gases. In two-stage systems, organic contaminants are volatilised from soil at lower temperatures (up to 600^0C) and are then treated in a second chamber (i.e. thermal or catalytic oxidation processes). Some relatively volatile inorganic contaminants (in particular mercury) may be recovered by

thermal desorption systems, which use condensation to treat the off-gases produced by heating. A possible categorisation is that one set of processes produce a slag or ash as a treatment residue, while a second set of processes produce a residual material, which is still soil-like. Thermal treatments are not applicable for most inorganic contaminants, which remain in residues such as fly-ash. Thermal processes use a variety of heat sources such as heated air, open flame and liquid heat-transfer, which can be via direct or indirect contact with the contaminated soil. Most known organic contaminants can be destroyed, but dioxins require high incineration temperatures. Furthermore, for any thermal process, dioxins can be formed when chlorinated organics are incinerated at low temperatures, and the reformation of dioxins in exhaust gases is also a possibility without rigorous process control. The most common applications of incineration methods are rotating oven, where incineration occurs at a temperature between 1200 and 1400 ^{0}C. For a fluidised bed, air is blown through the bed containing the soils to be incinerated, sand and calcium, the incineration residuals, are separated from the residue using a cyclone temperature between 800-900 ^{0}C but it can be run at 1200-1400 C^0 [Contaminated Land Rehabilitation Network, 2002]

1.2.2.2.5 Biological Treatment (bioremediation)

The objective of a biological remediation process is the degradation of contaminants to harmless intermediates and end products. The ultimate aim is the complete mineralisation of contaminants to carbon dioxide, water and simple inorganic compounds. A large number of organic contaminants can be degraded by micro-organisms and most biological treatments attempt to optimise conditions for degradation by the naturally occurring indigenous microbial population. Achieving these optimum conditions may require control of temperature, oxygen or methane concentrations, moisture content and nutrients. Biological degradation processes can be either *in situ* or *ex situ* and either aerobic or anaerobic.[Aulenta et al.,2005; Goi et al.,2006].Biological treatments have considerable scope for integration with other remediation processes and are applicable to both contaminated soil and groundwater. An advantage of the simpler biological treatments is their potential to be cost effective although long treatment times may be necessary. The presence of certain contaminants such as pesticides or heavy metals, however, may inhibit the effectiveness of biological treatment. An additional problem is the possible creation of more hazardous intermediate products. A range of biodegradation processes is available and methods of classification vary. The main groups include:

***In-situ* processes**—involving the injection of air or water to convey oxygen and possibly nutrients into the underground-contaminated mass.

Dynamic *ex situ* processes-following extraction, dynamic processes, in addition to the control of water, nutrients, etc. are applied to the soil and encourage rapid degradation. Processes include land farming, windrow turning and bioreactors [Hester and Harrison 1997].

Static *ex situ* processes-following extraction, the material is left undisturbed for the duration of the treatment, possibly under a liner. The condition of the material can be monitored with addition of water, nutrients and air to help microbial growth. The main static process is soil heap bioremediation, sometimes referred to as bio-piles and composting.

Phytoremediation- these processes use higher plants to degrade contaminants, to fix them in the ground, to accumulate within plant tissue or to release them to the atmosphere [Lei Yang 2008] Phytoremediation methods can be applied to achieve a range of remediation functions for both metal contaminants and organic contaminants which can be further classified as follows:

1. **Phytoextraction**- the uptake of metal contaminants in the soil by plant roots,
2. **Rhizofiltration**- the adsorption or precipitation of metal contaminants in solution onto plant roots.
3. **Phytostabilisation**- the use of plants to immobilise metal contaminants in the soil and the groundwater absorption and accumulation by roots, and
4. **Phytodegradation**- the breakdown of organic contaminants external to the plant through the effect of compounds produced by the plant.

Phytoremediation is based on the fact that a living plant can be considered as a solar-driven system that can extract and concentrate toxics elements form the contaminated soil. As clarified by Barter [1999] this involves principally three process: 1) phyoextraction involving extraction of heavy metals from soils; many wild plants concentrate high amounts of heavy metals in their foliage; 2) phytofiltration (or rhizofiltration) involving aquatic and semi-aquatic plants in various water purification systems; 3) phytovolatilzation involving volatization of some toxic metals e.g. Se, As and Hg. Maiti et al [2004] classified phytoremediation into the following basic techniques: rhizofiltration, phytoextraction, phytotransformation, phytostimulation and phytostabilization. Recent studies have demonstrated that microbes might be used to remediate metal contamination by removing metals from contaminated water or waste streams, sequestering metals in

soils and sediments or solubilizing metals to aid in their extraction. This is primarily accomplished either by biosorption of metals or enzymatically catalyzed changes in the metal redox state. Bioremediation of metals is still primarily a research problem with little large-scale application of this technology [Lovley and Coates, 1997]. A review by Adeniji (2004) indicates that many bacterial and fungal strains can assist with lead removal. Environmental organisms e.g. *Pseudomonas marginalis*, *Plectonema boryanum*, and *Desulfosporiosinus orients* can all biosorb lead [Malik, 2003]. This suggests that bioremediation using microbes is a practical alternative to biosorption removal of metal contaminants from industrial sites. The advantages and disadvantages of biological treatments are given in Table 1.10.

Table 1.10 The main advantages and disadvantages of biological treatment [Hester and Harrison.1997]

Advantages.	**Disadvantages**
Applicable to both contaminated soil and groundwater. Potential for integration with other processes. Simple processes can be cost effective. High contaminant specificity is possible.	High cost of complex processes. May require long process times. Possible formation of hazardous intermediate products. Presence of some contaminants may inhibit degradation. Most inorganic contaminants may not be treatable. Some complex organic contaminants may not be treatable.

1.2.2.2.6 Selecting the Best Practicable Environmental Option

The remediation strategy determined for a particular site should be capable of removing any actual or potential threat to the environment and of reducing any risks associated with the contamination to an acceptable level. However, in addition to offering the necessary degree of protection, the strategy should be practical and meet cost requirements.

Harris in CIRIA [1995] and Bardos et al [1994] have identified various factors to be considered when selecting remedial methods. Additionally, the Department of the Environment and National Rivers Authority have funded the production of guidelines for the evaluation and selection of remedial measures. Factors to be considered include:

a) applicability , effectiveness, limitations,
b) costs, development status, availability,
c) operational requirements, information requirements,
d) monitoring needs, potential environmental impact, and health and safety needs, post-treatment management needs.

Factors affecting the selection of the method of remediation design, and performance of remediation methods include the following: treatment objective(s); waste characteristics; type of process(es); waste management plan; regulatory compliance and costs.

1.2.2.2.6.1 Applicability

The remediation process has to be applicable to both the contaminants and the contaminated medium, be they soil particles, groundwater or the soil atmosphere. The remediation process must be able to reach the contaminants and the contaminants must be available, in a form that is available to the process. In practice, few processes are universally applicable and it may be necessary to use a combination of processes to achieve the desired level of remediation.

1.2.2.2.6.2 Effectiveness

Long-term effectiveness should be a major criterion in the evaluation and selection of any remediation process. The remediation process must be capable of achieving the level of treatment and risk reduction required. With engineering-based methods, effectiveness may vary with time as physical barriers may become less effective through deterioration and accidental or deliberate disturbance. With process-based remediation treatments, effectiveness could vary according to a number of factors such as the contaminant concentration, the type of soil, the feed rate to the process, the duration of treatment, etc.

Screening and treatability studies may be necessary to aid process selection and to determine optimum process conditions. Evaluating effectiveness during remediation is likely to require monitoring and quality assurance measures.

1.2.2.2.6.3 Cost of Remediation

The cost of remediation depends on many factors and may be broken down into mobilisation, operation (per unit volume or area treated), demobilisation, monitoring and verification of performance. Although data can only be tentative, comparisons of indicative equivalent costs may be a useful exercise at the early stages of consideration of different remediation options. Table 1.11 provides a range of indicative unit price costs for soil remediation in the UK [Contaminated Land Rehabilitation Network, 2002]. However, it is essential that site-specific factors be considered when estimating remediation costs for a particular site.

1.2.2.2.6.4 Availability

The availability of particular remediation processes will depend to some extent on the development status of the process and also on the market demand for it. When considering an appropriate technology it is normal to examine case studies where the process has been used successfully before. If a technology has only had restricted prior use then this, in turn, may limit its availability, as vendors experience difficulties in marketing untried processes. Consequently, although some processes are available and have been used overseas, their availability and application in the UK may be considerably less.

1.2.2.2.6.5 Health and Safety Considerations

All remediation methods require some degree of health and safety provision during their execution. However, requirements will depend on the hazards of the contaminants present on site, and the type of remediation being employed. The UK HSE has produced guidance for the protection of workers and the public during the development of contaminated sites and also a discussion paper on occupational hygiene aspects associated with different treatment types [Health & Safety Executive, 1996] up dated in 2006.

1.3. Stabilisation Materials

In This study uses Conner's [1990] definition of stabilisation which is a treatment with a stabiliser that has a buffering capacity and forces the system pH towards values at which the solubility of certain heavy metals is minimized.

1.3.1 Stabilized Materials and Waste Re-Use.

Cement and hydrated lime ($Ca(OH)_2$) and other pozzolanic materials such as fly-ash have been widely and successfully used for the stabilisation of arsenic [Singh and Pant 2006]. Alkaline matrices such as $Ca(OH)_2$, and Ordinary Portland cement (OPC) are commonly used in waste conditioning because they are inexpensive, have an extensively documented history of use and draw upon readily-accessible technology. Their alkalinity greatly reduces the solubility of many inorganic toxic or hazardous inorganic wastes, and inhibits microbiological processes. Moreover, since these matrices require water for hydration, they readily incorporate wet wastes Glasser [1997]. The US EPA has attempted to experimentally define the waste form performance quantitatively in response to the four binding constituents: OPC, fly-ash, blast furnace slag and clays, and to different combinations and concentrations of phosphate salts. Results indicated that the use of blast furnace slag and fly-ash increased the allowable salt loading in cement, but the use of clays resulted in forms with unacceptably low compressive strength (<35 bar).

Table 1.11 Indicative cost of remediation for the UK [Contaminated Land Rehabilitation Network, 2002]

Remediation Technology	Cost
Engineering capping	£ 15-£30/ m^2
Excavation and disposal to landfill	£50/ m^3
Encapsulation (shallow cut-off wall)	£ 40 - £ 60/ m^2
Encapsulation (deep cut-off wall)	£70 - £ 120/ m^2
'Typical' landfill gas control system	£ 00,000 per site
'Typical' grout curtain/ vent trench	£ 220,000 per site
Bioremediation	£ 35 - £ 45/ tonne
Vitrification	£ 40/ tonne
In situ vitrification (5t/hr)	£150 - £ 215/ tonne
Incineration (special wastes)	£750 - £ 1,000+/ tonne
De-chlorination	£100 - £ 300/ tonne
Soil vapour extraction	£40-60/ m^3 vadose zone
Soil washing	£30 - £ 35/ tonne
Enhanced thermal conduction	£35 - £ 45/ m^3
Six phase heating	£20 - £ 30/ m^3
In-situ chemical oxidation	£40 - £ 80/ m^3
Pump and treat	£ 20 - £ 30/ m^3
Free product recovery	£10 - £20/ m^3 vadose zone
Air sparging	£45 - £55/ m^3 groundwater
Oxidation of cyanide	£400/ tonne
Solvent extraction and incineration	£400/ tonne

1.3.2 Metal and Inorganic Constituents

With metal and inorganic constituents many factors and mechanisms must be considered, the most important of which are: pH control, chemical speciation, and redox potential control. Adsorption may also play an important role in stabilisation of metals, but there are little data in the literature to clearly distinguish adsorption from other mechanisms [Singh and Pant 2006].

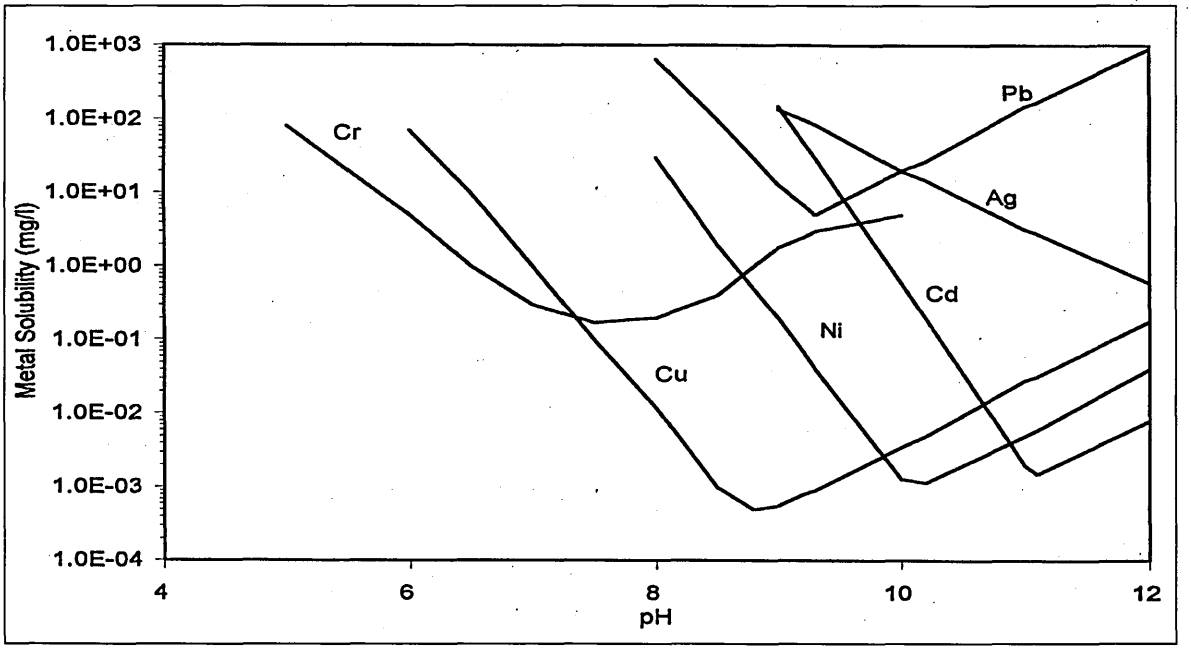

Figure 1.2. Metal hydroxide solubility vs pH. (From Conner and Hoeffner, 1998 a].

The efficiency of any system used to stabilize mobile metals is usually a function of its pH value within its environment, because the solubility of the most common metal species in S/S - hydroxides - is a function of pH [Wang, et al, 1996; Singh and Pant 2006]. In general, pH increases with addition of these highly alkaline reagents. However, the pH in question is not the natural value of the waste form but its final value after being subjected to a leaching test. That value, in turn, depends on the total alkalinity of the waste form. Most metal hydroxides exhibit a minimum solubility at some pH in the alkaline range, increasing in solubility as pH moves in either direction from that point. This behaviour is ascribed to the amphoteric behaviour of the species and is shown graphically in Figure 1.2 which shows, for example, that the optimum pH for minimum solubility of cadmium and nickel is 11.2 and 10.2, respectively. However, the solubility value for mixtures of metals will be a compromise because no two metals have solubility minima at the same pH. One way to

compensate for this is to study the distribution of metal species whose solubilities are relatively insensitive to pH value, for example, sulphides.

In addition, the hydroxide of certain metals, such as lead, exhibit solubilities above the current TCLP (Toxicity characterised leaching procedure) limit even at optimum pH. It should be noted that the pH of interest is not really that of the waste form itself, but of the leaching solution after extraction [Cobb et al., 1998]. In many cases, even at their minimum, pH values are not sufficiently low for effective stabilisation but, fortunately, metals in solution can usually be re-precipitated in a desired compound by controlling additives and precipitation conditions. Sulphides and silicates are very low-solubility species, and as such seldom need further treatment to meet S/S requirements {Bone et al 2004]. However, metal hydroxides are important for another reason: they have low-solubility and to completely re-speciate hydroxides would require their dissolution and re-precipitation, a technique that is hardly feasible.

However, a major problem with hydroxides (and some other low-solubility species) is that, for dissociated solid metal compounds, the concentration of the compound in the waste does not affect the concentration of metal ions in the leaching solution, so long as any solid metal species exist in contact with that leaching solution. Of course, the quantity of solid present will affect the long-term leaching behaviour of the waste form. Because the solubility product is constant if an anion, e.g sulphide S^{2-}, is added to a system containing lead hydroxide, in order to precipitate lead as a sulphide, more lead will dissolve. This will continue until all the $Pb(OH)_2$ has dissolved and been re-speciated to desired compounds by additive and precipitation conditions. However, the process is not immediate (i.e.it is kinetically limited) [Conner and Hoeffner,1998a].

In theory, metal hydroxide formation can be described as:

$$M^{z+} + n(OH)^{-1} = M_z(OH)n^{(z-n)} \qquad (1)$$

$$[M_z(OH)n^{(z-n)}] = {}^{\vee}\beta_{(OH)n}[OH^{-1}][M^{z+}], \qquad n = 1, 2, \ldots \qquad (2)$$

Where $M_z(OH)n^{(z-n)}$ and M^{z+} are metal hydroxide and free metal ions, respectively,
${}^{\vee}\beta_{(OH)n}$ is an overall formation constant for metal hydroxide, and
n is the number of hydroxide ions associated with each metal ion.

Following Apak and Hizal [1999], the solubility of metal oxides and hydroxides can be described as:

$$P[M^{z+}] = -\log[M^{z+}] = -\log {}^{c}Kso - z\,pKw + z\,pH \quad (3)$$

$${}^{C}K_{so} = [M^{z+}][OH^{-}]z \quad (4)$$

Where ${}^{C}K_{so}$ is the conventional solubility product based on the levels of individual metal ions given by $cKso = [M^{z+}] + [OH^{-}]$, [Lo et al., 2009].

1.3.3 Cement Systems

The treatment of hazardous wastes using cement-based S/S is increasingly important as an option for remediating contaminated sites. Indeed, among the various treatment techniques, S/S is one of the most widely used methods for treating inorganic wastes [Paria and Yuet, 2006].

As with other methods of S/S, cement-based S/S is a process in which (usually) OPC with added water reacts with waste components to form a chemically stable solid with a degree of mechanical strength. Essentially the waste is bound together and stabilised by the concrete formed [US EPA 2009]. This relatively simple approach is now being used to treat an extensive variety of wastes containing many types of contaminants, including: metals, organics, organo-metallics and soluble salts [US EPA 1999; Silveira et al., 2003].

[Malviya and Chaudhary 2006] reported that Cement-based S/S has been widely used for about 50 years. The overall process of cement hydration includes a combination of solution processes, solid-state reactions and interfacial phenomena and is extremely complex, particularly in the presence of heavy metals. The correct selection of cements and operating parameters depends upon a proper understanding of the chemistry of the S/S process [Chen et al 2009]. Liu et al [2008] used the S/S technology to treat contaminated soil in UK and reported treatment using OPC or EnvirOceM, ACT (accelerated carbonation technology) caused increase in the PI (plasticity index) of the treated soil and made it more stable during long-term weathering.

While numerous formulations have been used for the stabilisation process, the most common practical binder material for S/S is OPC, which can be combined with fly-ash, lime, steel blast furnace slag or clay, either to reduce cost or enhance final product performance.[Moncef and Amjad, 2007]. Using pozzolanic products and cementitious by-products can enhance the long-term strength and impermeability of the stabilized system. Partial replacement of OPC with pozzolanic material such fly-ash, or steel slag, results in

the consumption of calcium hydroxide and alkalis during the pozzolanic reaction [Moncef and Amjad, 2007].

Early in the 19th century, cements were developed which would achieve both higher compressive strengths than lime-based products and, set and gain strength in the presence of excess water. The most important was called Portland cement, due to its resemblance to stone from that area, and this is now manufactured worldwide: production exceeds 10^9 tonnes per year. Portland cement is made from raw materials which are blended and reacted, usually in a rotary kiln, at temperatures exceeding 1400°C. The chemical composition of Portland cement in oxide weight %, is; CaO: 61-67, SiO: 17-24, ZO: 3-8, FeO: 1-6, MgO: 0.1-4, with a trace of NaO and KO at about 1.5%. [ASTM C150.USA]

Ordinary Portland Cement (OPC) is defined by the European Standard EN197.1, as a hydraulic material, which consists of at least two-thirds by mass of calcium silicates $3CaO.SiO_2$ and $2CaO.SiO_2$, i.e. the ratio of CaO to SiO_2 should not be less than 2.0. The remainder consists of aluminum and iron-containing clinker phases and other compounds, [Taylor, 1997]. OPC is manufactured by blending the raw materials in a rotary kiln, at a temperature of about 1450°C. The resulting calcined product, termed clinker, is finely ground prior to use, normally to a specific surface density of about $4000g.cm^{-2}$ [Popescu et al ., 2003].

Lee [2005] has experimentally investigated the different types of cement used for the stabilisation of metals, and concluded that calcium hydroxide and silica with traces of FeO and MgO were present.

According to Glasser [1997], mineralogically, Portland cement clinker consists of four principal phases; which have idealised compositions close to Ca,SiO, Ca,Al,O, and Ca,(Al,Fe)O, free lime, CaO, normally comprising less than 3% of the clinker. Wilk [2009] comments that cement is frequently selected for its ability to act as a reagent which (a) reduces the solubility of hazardous constituents by chemically fixing them, (b) binds free liquids by various chemical processes, (c) lowers the permeability of the waste, (d) encloses waste particles within an impermeable coating, and (e) helps reduce the toxicity of some of the contaminants. These are accomplished by both physical changes to the waste form and, often, chemical changes to the hazardous constituents themselves. The chemical change occurs in the concentration of leaching, which is assessed by a chemical method known as the leaching test. The physical change mainly appear in the performance

standard measured by the paint filter test (pass/fail), hydraulic conductivity (<1X10^{-5} cm/sec), and unconfined compressive strength (0.34 MPa (>50 psi)), which is according to US EPA guidance.

1.3.3.1 Chemistry of Hazardous Metals in Cementitious S/S Wastes Contact

A cementitious material is one that hardens when mixed with water. Studies by Cocke et al. [1991] have provided insight into the chemical binding and interactions between hazardous metal substances and Portland cement. Specifically, priority metal pollutants such as barium, cadmium, chromium, lead, mercury, and zinc were studied to determine models for the interaction of each metal with the cement matrix [Cobb et al., 1998].

The significant role in the immobilisation process is attributed to the so-called C–S–H phase (calcium silicate hydrates) - the main component of hardened paste. Absorbability and low permeability prevent the migration of liquids, and the presence of small gel pores (micropores) are among the critical factors affecting the high immobilisation potential of C–S–H. Zbigniew et al [2009] have reviewed the effect of OPC with added slag or fly-ash and found the metals are successfully stabilized and chemically formed. They found barium present in the form of its sulphate and/or carbonate, while mercury was present as a surface particulate, HgO. Chromium was found to incorporate itself into the C-S-H matrix. Cadmium, lead and zinc formed mixed hydroxides and adsorb to the surface at high pH. That Zn on the outer surface is effectively removed by acid attack was confirmed by leaching tests. For metals deposited in mixed hydroxide form on the surface of the cement particles, prior mixing with a suitable phosphate, e.g. TSP (triple super phosphate), would lead to the formation of a highly insoluble metal phosphate which, when deposited on the surface of the particle, would be significantly more resistant to any subsequent leaching. However, Chen et al[2009] reported that according to the decomposition rate of minerals, heavy metals accelerate the hydration of tricalcium silicate (C_3S)(Ca_3SiO_5) and Portland cement, although they retard the precipitation of Portlandite due to the reduction of pH resulted from hydrolyses of heavy metal ions. The chemical mechanism relevant to the accelerating effect of heavy metals is considered to be H^+ attacks on cement phases and the precipitation of calcium heavy metal double hydroxides, which consumes calcium ions and then promotes the decomposition of C_3S (Ca_3SiO_5).

Batchelor [2006] concluded that contaminants are stabilized by a wide variety of different types of reactions such as precipitation or chemical inclusion, adsorption, and absorption

but most of them are strongly affected by pH. Therefore, contaminant release is strongly affected by changes in pH value. Coleman et al [2005] investigated the interaction of aqueous Pb^{2+} ions with crushed concrete fines (CCF), and showed that the surface of Pb–CCF was generally composed of a network of lead-carrying calcium silicate. Removal of Pb^{2+} from the solution took place as result of diffusion of the lead into the cement matrix. Coleman and his colleagues suggested that the underlying mechanism was one-for-one replacement of the Ca^{2+} by Pb^{2+} in the C-S-H lattice. This is possible because the two atoms are of a similar size and can take place without disrupting or changing the crystal structure of the mineral. Evans [2008] has proposed that the rare, calcium-rich, heavy metal-bearing polygons observed on the surfaces of each of the recovered CCF specimens were re-precipitated Portlandite crystals, distorted from their normal hexagons by the inclusion of Pb^{2+} ions. Gougar et al [1996] reported that Pb^{2+} could replace Ca^{2+} in ettringite, but not in the C-S-H structure where Pb is immobilized by precipitation as hydroxide and carbonate. Thomas et al [1981] and Jing et al [2004] suggest Pb stabilization in cement-treated materials can be attributed to fast precipitation of lead compounds at the surface of colloidal materials during cement hydration. From this study the suggestion is precipitation of lead occurred as results of increasing the pH during mixing with OPC.

Van der Sloot [1997] and Kumpiene et al [2008] have reported that the amphoteric nature of lead makes it difficult to immobilise in cement-based waste forms. Lead is fairly insoluble in the hydroxide form between pH 7 and 12. Thus control of pH is an important factor in improving lead retention in the waste form. Wiles and Barth [1992] have reported the effect of OPC on lead solutions with increase in the pH of the solution, to a pH level of 12.2. The concentration of lead solutions with pH has been reported by Dongjin [2007] to a pH level of 12.8. Conner [1990] has investigated this phenomenon to a pH level of 13. All researchers agreed that pH has a major role in mobilising metals.

During the mixing of OPC with DI water there was an increase of the pH and consequent chemical reactions, described by Dongjin [2007] in the following equations:

$$3CaO.SiO_2 + H_2O \rightleftharpoons 3Ca^{2+} + SiO_4^{4-} + 2OH$$

$$3CaO.Al_2O_3 + 6H_2O \rightleftharpoons 3Ca^{2+} + 2Al_3(OH)_4^{-} + 4OH^{-}$$

Thevanin and Pera [1999] have reported and Chatelet et al [1995] have confirmed that Pb-C-S-H occurs as soon as tricalcium silicate Ca_3SiO_5 (alite, C3S) begins to hydrolyze. The Pb-C-S-H is referred to as a C-S-H of regular stoichiometry where lead replaces calcium. Others state [Paria and Pak 2006] that lead fixation is due to a double phenomenon: first the precipitation of a metallic hydroxide and then encapsulation of this compound in the C-S-H phase. For example, Bishop [1986] submitted a lead-polluted cement sample to sequential extraction and found that the lead is bound together with Ca, Si, and to a lesser extent Fe and Al. However according to Birss and Waudo [1989] the following reactions occurred in the early stages when the pH level was increased from 9 to 14 using NaOH:

$$Pb(OH)_2 \rightarrow PbO + H_2O$$

$$Pb + 2OH^- \rightarrow PbO + H_2O + 2e^-$$

$$2\,Pb + 2OH^- \rightarrow H\,PbO_2^-$$

Barna et al [2005] expected the dissolution of alkaline metals to be independent of pH, whereas calcium solubility decreases as pH increases and becomes very low for a pH > 12 (Portlandite-like behaviour). Also it is reported that the behaviour of lead and cadmium (amphoteric metals) strongly depends on the leachate pH, with a maximum Pb release for the pore water pH >12. Dong-Jin [2006] showed that the rise in pH of the leachate occurs due to the dissolution of the cement matrix, which consists mainly of $Ca(OH)_2$ (Portlandite) and calcium–silicate–hydrate (C–S–H). Conner [1998] and Kumpiene et al [2008] have reported that Ca compounds are generally efficient for lead immobilization, which is mainly caused by an increase in soil pH. Since soil pH might not be stable and acidification would lead to lead release, application of Ca compounds alone might not be sufficient for a long-term lead immobilization. Alkaline compounds are more useful if used as supplements to neutralize soil acidity caused by other amendments, e.g. phosphoric acid.

When Portland cement is mixed with water, the initial hydration reaction results in a fast accumulation of calcium in the soil. The clay soil was then effectively stabilized as calcium ions were released from the mixture. About twelve hours after placing the OPC into the soil the amount of calcium decreased and C-S-H and $Ca(OH)_2$ were produced. The calcium in the cement met the soil's initial needs with unbound cement present until the calcium was fully used [Li and Deng-Fong, 2009].

Chrysochoo and Dermatas [2006] also reported that immobilization of chromium and selenium was due primarily to sorption and inclusion in hydrated-calcium–silicates (CSH), as their solubility curve followed the characteristic pH values of CSH dissolution, not those of ettringite. Similarly, the leaching behaviour of arsenic and lead could not be directly linked to ettringite dissolution, because there was no clear evidence that substituted ettringite had formed in the cement pastes.

Muralidharan et al [2005] has stated that water-soluble chloride alone is a good indicator of the concentration of chloride ions in concrete, that chlorides may either be chemically bound in compounds like Friedel's salt ($3CaO{\cdot}Al_2O_3{\cdot}CaCl_2{\cdot}10H_2O$) which can be formed in cements initially rich in C3A and C4AF in which chloride ions have replaced sulphate ions. However the sulphates in the cement form stronger bonds than the chlorides, so only a fraction of the original content of C3A and C4AF is accessible for chloride binding. Justnes [2001] in referring to the work of Lambert et al [1985] and Holden et al [1983] where the chloride binding of the cement paste was shown to increase with increasing C3A, concluded that the amount of free chloride decreased with increasing C3A, and that the amount of bound chloride decreased with increasing concentration from the cements. The replacement of cement by ground blast furnace slag or the addition of fly ash increases the chloride binding since these mineral additives form additional calcium aluminate hydrates in their reaction, while silica fume replacements will decrease the chloride binding. Ryou and Ann [2008], extending the work of Potgieter and Marjanovic [2007] has reported that the release of Cl bound in cement will be achieved only by using nitric acid which means that this Cl is unlikely to be soluble in the pH levels likely to be found in practice.

1.3.4 Lime Systems

Lime and other high alkalinity materials are widely used to reduce the solubility of heavy metal contaminants in water.[Mickney et al 2001] Here, 'lime' is used to mean calcium hydroxide, calcium oxide or calcium carbonate. However, calcium oxide has a strong exothermic reaction with water, which has an additional effect of drying the soil; the effect of lime is similar to the effect of calcium hydroxide on soil and clay.

In the past twenty years, the application of lime has been extended to the treatment of contaminated waste containing reactive aluminium or siliceous components, and stabilisation of contaminated soils prior to use for construction purposes [Reid and Brookes 1999]. Although not systematic, research in Japan has endorsed the effectiveness of lime

stabilisation of heavy metal wastes, as well as its potential for re-use of the treated waste as a construction material [Boardman,1998; Dermatas and Meng, 2003] It has long been known that lime can be used to modify the plastic properties of soils[Robinson and Burnham, 2001].

Lime has been used in many parts of the world for the stabilisation of laterite roads, and by thousands of waste generators in the USA, and elsewhere, [Wong and Selvam 2006] who found that excess lime would neutralise acidic wastewater and meet leaching test standards , which also had the benefit of precipitating metals before discharge. In most cases, the addition of sufficient lime for fixation would raises, the pH of the effluent above that acceptable for discharging or recycling to treat the effluent and so this stage becomes a separate step in the process. Lime can be added either before the effluent enters the sludge conditioning tank for filtering or, as a separate step, after filtration on the way to the filter cake. Lime, along with other additives, is used in most central waste treatment facilities, as a neutralisation and stabilisation agent for sewage sludge, primarily for odour control and pathogen reduction [Conner and Hoeffner, 1998a].

1.3.4.1 Quicklime S/S Treatment Principles

The pH of natural soil deposits are typically in the range of 5–8. However, when a substantial proportion of lime is added to soil-fly-ash, the pH of the mixture rises to approximately 12.8, the same pH as that of saturated lime water. At this elevated pH level, the solubility of the silica and alumina present in fly-ash and clay minerals is greatly increased. This makes them available to react with the calcium in the lime and/or fly-ash, to form calcium and alumina silicate hydrates (CAH and CSH), C = CaO, S = SiO_2, A=Al_2O_3, and H=H_2O. It is commonly believed that the formation of these cementitious hydrates is the major reason for the high strength and low swell of the treated solids and immobilisation of heavy metals (through surface sorption, inclusion and physical entrapment). The three equations given below are a simplified, qualitative representation of some typical soil-lime (pozzolanic) reactions [Dermatas, and Meng,2003]

$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^-$

$Ca^{2+} + 2OH^- + SiO_2$ (Clay Silica) $\rightarrow$ C-S-H ($3CaO \cdot 2SiO_2 \cdot 4\ H_2O + 3Ca(OH)_2$ Calcium Silicate Hydrate)

$Ca^{2+} + 2OH^- + Al_2O_3$ (Clay Alumina) $\rightarrow$ C-A-H ($Ca_2Al(OH)_6$ (Calcium-Aluminate-Hydrate)

Depending on reaction conditions such as soil characteristics, quantity and type of lime, curing time and temperature, a wide variety of hydrate forms can be obtained. The alumina

liberated from the solids may combine with sulphates in the soil and/or groundwater to form a series of calcium–aluminate–sulphate hydrate compounds, possibly to the formation of ettringite, $[Ca_3Al(OH)_6]_2(SO_4)_3.26H_2O$. Ettringite has a needle-like crystal structure based on parallel columns of material of empirical composition $[Ca_3Al(OH)_6.12H_2O]^{3+}$. Between the needles are channels which contain sulphate ions and the remaining water molecules. [Dermatas, and Meng,2003]

It has been claimed by [Mickney et al., 2001] that lime processes in general, are not as effective as cement-based systems in reducing leachability of metals. The reasons given are the very high pH that often results from lime-based systems, and that these pozzolanic processes do not bring metals, such as chromium and lead, into the silica matrix as effectively as cement. However, each waste and disposal problem must be evaluated on its own merits, and lime/fly-ash may provide acceptable leaching results in many S/S processes. Sprynskyy [2009] has used lime successfully to reduce the leaching of heavy metals in sludge.

However, many researchers have studied the release of metals from soils such as, Masahiro and Wada. [2007] who reported that heavy metal cations released from functional groups in acid solutions are re-adsorbed as exchangeable cations by layer silicate minerals. In this study at low pH (1.2) there was no change in the pH of the final solution. The pH of the washing fluid plays a significant role in the extractability of heavy metals from soils. Dermont et al [2008] reported that several mechanisms contribute to the extraction of metals from soil using an acid solution: (1) desorption of metal cations via ion exchange; (2) dissolution of metal compounds; and (3) dissolution of soil mineral components (e.g. Fe–Mn oxides), which may contain metal contaminants. At low pH, the protons (H^+) added can react with soil surface sites (layer silicate minerals and/or surface functional groups including, e.g. Al-OH, Fe-OH, and COOH groups) and enhance desorption of metal cations, which are transferred into the washing fluid.

The pH level is one of the most important chemical parameters influencing leaching of contaminants from waste material, and the pH of soil, or contaminated material has a major influence on the solubility of contaminants by influencing the degree of ionization and subsequent overall charge Bone et al [2004]. In leaching experiments the pH is determined by a number of possible reactions such as production of CO_2 as a result of biological activity and dissolution of atmospheric CO_2, and many metals are known to leach more

rapidly at extreme pH values [Van der Sloot et al., 1997; Jang Y et al [2002]; Townsend and Jang [2003]. Also CO_2 interacts with cementitious wastes when calcium in the waste reacts with the CO_2 to form calcite ($CaCO_3$) Pereira et al [2007].

1.3.5 Magnesia Systems

According to Warren [2006], magnesium oxide, or magnesia, is a white mineral that occurs naturally as a periclase and is a source of magnesium. Its chemical formula is MgO and is easily made by burning magnesium in air, which readily oxidizes with a bright white light, resulting in a powder. Care must be taken to protect the poowder from moisture as it is hygroscopic. Magnesium hydroxide is formed in the presence of water ($MgO + H_2O \rightarrow Mg(OH)_2$), but the process can be reversed on heating.

Commercially, magnesium oxide is formed by heating magnesite ($MgCO_3$) to 600-800°C, which drives off most of the CO_2. It has good thermal conductivity and electrical resistivity at elevated temperatures. The presence of CaO in the magnesia is generally low, but if it is present then the mineral is called magnesite ($MgCO_3$), like sea water magnesia. Magnesia consists of about 87% Mg (by weight), but this varies depending on the grade of magnesia and purpose of use. To date there has not been sufficient research into the use of MgO as a stabilizing material, but it has many other applications; e.g. absorbent, animal feedstuffs, catalyst, catalyst support, fertilizers, gas-scrubbing equipment, magnetron sputtering sources, special cements, refractory materials and for use in the preparation of a variety of magnesium chemicals [Mark 2006].

The manufacture of vitirifed clays and concretes both release process emissions and in the case of calcite materials used in concretes, chemically bound CO_2 [Harrison 2008a]

Magnesia Brucite

$MgO + H_2O \rightarrow Mg(OH)_2$

Caustic magnesia produced from the calcination of magnesium carbonate is an inexpensive product where magnesium oxide is the main component. As an active treatment reagent, although it is more expensive than lime, caustic magnesia raw material produces less waste, is less hazardous, and is therefore cheaper to handle [Younger et al., 2002]. It also retained Zn, Cu, Pb and Mn in permeable reactive barriers by increasing the pH of

contaminate which subsequently caused precipitation and retention of the metals. [Cortina et al., 2003].

Brucite will maintain the pH of a solution at around 10 - 11 for much longer periods than Portlandite, as for most kinetic pathways its carbonates are much less readily soluble, mobile or reactive. The solubility product of brucite at 1.8×10^{-11} is much lower than that of Portlandite at 5.5×10^{-6}. [Harrison 2008a].

There are many advantages in using MgO as a raw material: magnesium oxide has minimal environmental impact, low solubility, and high alkalinity, reaching a maximum pH of 10, which helps to neutralize acids and precipitate metals [Teringo,1987]. However, due to its high cost, pure MgO is 8–10 times more expensive than the equivalent grade of lime, it is a feasible alternative only if low-grade magnesia is used for removing heavy metals [García et al., 2004]. Nevertheless, it is possible that magnesia could be used instead of cement for soil S/S. If MgO is introduced into soils it reacts with the soil moisture to yield brucite and helps to maintain a pH level of about 10.52 in water (Harrison,2008a), which favours retention of lead ions by soil colloids and precipitation of carbonates and hydroxides of lead. Additionally, MgO reacts with silicic acid to form phyllosilicates at normal soil temperatures, and these may fix lead in their interlayer spaces or in octahedral sites [Ono and Shin–Ichiro, 2006].

Sundarama et al.[2008] have used MgO as an absorbent for removal of fluoride from water, but there are few known publications describing the use of magnesia for heavy metal stabilisation [Bone et al., 2004; Conner, 1990]. However some commercial reports in USA (http://www.magnesiaspecialties.com/waterinfo.htm) have compared different masses of various materials to have the same effect as $Mg(OH)_2$ in removing heavy metals

Table 1.12 Relative masses of various materials which have the same effect as $Mg(OH)_2$ in removing heavy metals

Substance	**$Mg(OH)_2$**	**Hydrated lime $Ca(OH)_2$**	**Caustic soda (NaOH)**	**Soda ash (Na_2CO_3)**	**Sodium bicarbonate ($NaHCO_3$)**
Relative amount (by weight) required.	1	1.27	1.37	1.82	2.80

1.3.6 Strength of the S/S Produced

Routinely, the proportion of cement used to solidify waste varies from 5% to 20%. Such a low proportion cannot adequately coat every individual waste particle but, nevertheless, still gives rigidity to the waste form, probably because of the physical changes brought about by the normal hydration process, the so-called "false set" mechanism - that is, precipitation of salts such as gypsum which gives additional structural strength. Solidified materials have a compressive strength, which varies according to the kind and quantity of the constituents forming the pore structure, but is typically <1MPa, and so are considered structurally weak. This quality depends on the cement hydration products and their reaction products with admixtures [Zivica. 1997]. The US EPA considers a S/S material with a strength of 0.35MPa to have a satisfactory unconfined compressive strength. This minimum guideline has been suggested to provide a stable foundation for materials placed upon it in a landfill. In the UK, the acceptable 28-day strength is 0.7MPa but values as low as 0.35MPa may be considered depending on the test specimen. [Malviya and Chaudhary, 2006].

1.3.7 Waste Materials and Waste Re-use

Research and development of new technologies and applications, especially alternatives to incineration, to deal with waste are constantly developing. These include building and construction materials, construction fill, drainage materials, landfill liners and covers, sorbents, etc. [DEFRA, 2008]. In addition, there is research into the re-use of waste material as raw materials, for example re-used wastes include shredded tyres, fly-ash, steel blast furnace slag, sewage sludge and demolition waste [Tabaa, 2008; WasteOnline, 2006].

1.3.7.1 Fly-Ash Systems

Waste materials are produced in large volumes at coal-fired power plants; direct combustion by-products include fly-ash, bottom ash, and boiler slag and, in addition, there are the products of the desulphurisation of the flue gas. These materials have been shown to have certain advantageous properties for engineering, construction and manufacturing applications.[Vom Berg and Feuerborn2005].

Fly-ash – so-called because it is transported from the combustion chamber by exhaust gases - is the finest of coal ash particles. It is a fine powder formed from non-combustible mineral matter in the coal, plus a small amount of carbon that remains from incomplete

combustion [United Kingdom Quality Ash Association, 2008]. Fly-ash is generally light tan in colour and consists mostly of silt-sized and clay-sized glassy spheres, giving it a consistency somewhat like talcum powder. Properties of fly-ash vary significantly with coal composition and plant-operating conditions. Fly-ash is captured either in an electrostatic precipitator or a fabric filter bag.

Fly-ash can be considered as either cementitious or pozzolanic. Possessing both cementitious and pozzolanic properties is what makes some fly-ashes useful for replacing cement in concrete, and many other building applications. Ten million tonnes of fly-ash are produced annually in the UK of which 1.5 million tonnes is re-used, mainly in construction related applications (e.g. replacement for cement, structural fill, grouting mixes, and mineral filler in asphalt paving). There are many areas that can be investigated for the re-use of ash including: production of zeolites, sorbents, glass and composite materials, absorption and waste stabilisation and also in agricultural applications.

In 2003, in excess of 120 million tons of Coal Combustion By-Products (CCBs) were produced in the USA from over 600 coals fired power plants [FlyAsh Direct, 2008], of which more than 72 million tons was fly-ash. Over 450 million metric tons of fly-ash is produced annually around the globe. A decade ago, in the EU over 90% of CCBs, including fly-ash, were recycled [Hester and Harrison, 1997], although usage rates vary significantly between EU nations. The situation is expected to have improved significantly since then.

PFA and FBA (furnace bottom ash) can be used in a variety of applications, many of which use binding, where the PFA is mixed with some form of binding agent such as cement, lime or bitumen. In such circumstance any potential for leachates is minimised by the nature of the binding agent, e.g. the PFA becomes part of a low permeability, high alkalinity system that is fully encapsulated. In such bound applications, leachates from the binders and/or aggregates may be significantly greater than from the PFA [United Kingdom Quality Ash Association, 2002]. Care should be taken when assessing data from such bound systems to ensure inaccurate assumptions are not made. The following are common applications for PFA:

Aerated concrete blocks – PFA forms the primary material within these types of blocks, which are widely used in house/office buildings. Again, they are considered one of the most environmentally friendly uses of a by-product like PFA.

Ready mixed and precast concrete – PFA classified or selected to BS3892 Part 1 or EN450 is widely used as an addition in concrete, partially replacing Portland cement. This reduces overall CO_2 emission by ~0.9 tonnes for every tonne of Portland cement replaced.

Grouting of mines and caverns – PFA is widely used for stabilising large voids in the ground, allowing it to be returned to productive use and ameliorating the blight of subsidence to housing, offices, factories, etc. PFA is preferred by grouting companies due to its superior properties in comparison with naturally occurring aggregates.

Fill and ground remediation – PFA has been extensively used for building embankments, restoring old quarries, etc, since the 1950's. Although this is an unbound use, there are no known environmental problems associated with the use of PFA in such applications.

There are four reasons to increase the amount of flyash being utilized, which are firstly, disposal costs are minimized; secondly, less area is required for disposal, thus enabling other uses of the land and decreasing disposal permitting requirements; thirdly, there may be financial returns from the sale of the by-product or at least an offset of the processing and disposal costs; and fourthly, the by-products can replace some scarce or expensive natural resources [Ahmaruzzaman 2010].

PFA also has great potential for use in a variety of applications, replacing naturally occurring aggregate, or as a pozzolanic binder, e.g. in road construction. The reduction of cost of solidification is the major purpose of incorporating PFA in cement based S/S processes but the lower pH level of PFA also reduces the possibility of generation of ammonia from wastes [Poon et al, 2001]. The pozzolanic character of fly-ash immobilizes heavy metals by the formation of a well-bonded, low porosity network of calcium silicate and aluminate hydrates that acts as a binding agent.[Srivastava et al 2008].

Kumpiene et al [2007] have suggested fly-ashes as possible solutions to treat problems related to acid mine drainage and metal solubility, as they can neutralize the pH of acidic soils, and render most cationic metals less mobile. Fly-ash also increases the surface area available for element adsorption, improve the physical properties of soil.

Both Qiao et al [2006] and Cote et al1987] found that the incorporation of PFA in the cement-based S/S system resulted in the lowest leaching of heavy metals. Alinnor et

al[2007] reported that at pH values between 4 and 6, Cu^{2+} and Pb^{2+} ions may be removed from solution by precipitation.

The use of fly-ash in a cementitious matrix lowers the overall alkalinity of the system and thus improves immobilisation of amphoteric metals compared to a purely cement system [Poon and Perry,1987]. PFA plays an important role in improving the retention of mercury in the cement matrix through sorption.[Poon et al, 2001].

Fitch and Cheeseman [2003] considered metal-plating waste treated by OPC and coal PFA that had been exposed to the environment in SE England for approximately 10 years. They found that the surface region of the solidified and stabilized waste was extensively carbonated and so had a reduced capacity for acid neutralization compared to samples taken from the bulk. In addition, the leaching properties of material tested after 28 days were very different from leaching determined in environmentally exposed S/S waste.

1.3.7.2. Ground Granulated Blast Furnace Slag

Blast steel slag is produced in millions of tons every year as a by-product of many industries, particularly metal smelting and coal processing. In 2004, the EU alone produced nearly 15 million tons of steel slag during the separation of molten steel from impurities in steel-making furnaces. Of this, 45% was used for road construction, 14% for internal recycling, 11% for landfill, 3% for fertilizer, 3% for hydraulic engineering and 1% for cement production [Euroslag, 2008]. Global slag production is about 50 million tons per year [Euroslag, 2008].

Steel slag will vary depending on the raw materials and process used. Intensive research work over three decades has meant that, today, about 65% of the steel slag produced has some useful application, but the remaining 35% is dumped [Motaz and Geiseler, 2001; Tsakiridis et al., 2008]. Because of its lower environmental impact, GGBFS is often included in the lists of recommended materials of many bodies whose function is to protect the environment, such as the EPA in the USA [EPA Report, 2009] and The European Slag Association. There is a long tradition in using the slag as potential secondary raw material in the construction industry and other fields. Recently much attention has been paid to the environmental impacts of the waste material. Jinying Yan et al, [2000] GGBFS is a by-product of the iron and steel producing industries and on a world scale some 50×10^6 tons per year of steel slag is produced. In Europe alone, 12×10^6 tons of steel slag is produced

annually. Depending on the country, up to 65% of this steel slag is re-used, but the remaining 35% is still dumped, and in recent years has become a significant problem in environmental engineering [Tsakiridis et al 2008; Geisele, 1996]. GGBFS is a waste product in the manufacture of iron composed mainly of calcium silicate and aluminosilicate. If allowed to cool slowly, it crystallizes to give a material having no cementing properties. If cooled rapidly, it forms a glass, which is a latent hydraulic cement, [Duchesne and Laforest 2004].

The enormous quantities generated, and the cost of disposal, has made the management of steel slag a significant issue in environmental engineering. Slag is a heterogeneous mix of oxides such as CaO, Fe_2O_3, SiO_2, Al_2O_3, and MgO. The relative proportions and quality of these oxides will change with different steel making processes, raw materials used, even the cooling . The heterogeneity of the resulting slag will affect its disposal - e.g. method of removal of heavy metal from the aqueous solution – as will the design of new methods of disposal [Xue et al 2009]. However, the calcium silicate hydrates contain less CaO than the calcium silicates in cement clinker, so calcium hydroxide is formed during the hydration of Portland cement. This is available for reaction with supplementary cementitious materials such as GGBFS and pozzolans. The simplified reaction with water may be expressed as:

$$2Ca_3OSiO_4 + 6H_2O \rightarrow 3CaO.2SiO_2.3H_2O + 3Ca(OH)_2$$

However, the adsorption capacity of GGBFS is pH dependent and the hydration of the slag composition should provide a high pH in aqueous solutions. According to Chaa et al [2006], Ahn et al [2003] and Nilforoushan and Otroj [2008] major hydration reactions may occur with calcium oxide, magnesium oxide, calcium silicates, and calcium aluminate as follows:

$$CaO + H_2O \rightarrow Ca(OH)_2; \quad (1)$$

$$MgO + H_2O \longrightarrow Mg(OH)_2; \quad (2)$$

$$2Ca_2SiO_4 + 4H_2O \longrightarrow 3CaO \,.\, 2SiO_2 \,.\, 3H_2O + Ca(OH)_2; \quad (3)$$

$$2Ca_3SiO_5 + 6H_2O \longrightarrow 3CaO \,.\, 2SiO_2 \,.3H_2O + 3Ca(OH)_2; \quad (4)$$

$$CaO \,.\, 7Al_2O_3 + 12H_2O \longrightarrow CaO \,.Al_2O_3 \,.6H_2O + 6Al_2O_3.\, H_2O : \quad (5)$$

Mishra and Patel [2009] used 2g of GGBFS for 100ml of metal concentration 50-100mg/l at optimum pH 6 and reported maximum removal of lead and zinc in the range pH 6-10, in

agreement with results in the subsequent chapters of this thesis. Curkovic et al. [2001] used 0.25-1 g of steel slag to remove Pb and Cu solution; they concluded the steel slag waste constitutes a good adsorption material for the removal of lead and copper ions from aqueous solution and wastewater.

Steel slag was found to be an effective adsorbent for Pb, Zn, Cd, Cu and Cr ions within the range of ion concentrations employed (blast furnace sludge of two different carbon contents and a metallurgical coke were used to adsorb lead ions from aqueous solutions. [Das et al 2007]. As Dimitrova [1996] has explained, the metal ions react with OH^- ions. As a result of the alkalizing ability of the material, metal ion adsorption takes place mainly in the form of hydroxo complexes. The high sorption capacity of the blast furnace slag is related to the formation of scarcely soluble compounds (silicates) on the sorbent surface. The complex nature of the interactions on the slag-solution system of metal ions, especially at high adsorbate concentrations, when conditions are created for hydrolysis produces polymerization, makes it difficult to interpret the sorption data and to determine correctly the thermodynamic parameters. This possible involvement of the silicic acid in the process of metal ion removal was perceived as a colloid-chemical component of the process. According to Nilforoushan and Otroj [2008] such an explanation is based on the concept of destruction - epitaxial conversion of the solid substances. That means new crystal growth with stats of polymers caused by adsorption process of Pb. Feng et al [2004] have reported that GGBFS was appropriate adsorbent for heavy metal removal from aqueous solutions. The slag combines ion-exchange and adsorption properties with an acid-neutralising ability. Iron slag has a much higher adsorption capacity for metals than steel slag because of its greater surface area, higher porosity and higher ion-exchange ability. Flotation following the slag adsorption could effectively separate the slag, yielding very low solution turbidity's.

Nilforoushan and Otroj [2008] and Yamashita et al [1983] have reported that the mechanism of adsorbing and fixing heavy metals by GGBFS is due to one or more of the following effects: adsorption, co-precipitation, hydroxide precipitation, sulphide and ion exchange, but the removal of lead cannot occur solely due to precipitation as hydroxide. Because of the nature of slag, it is difficult to determine which surface species (AlOH, AlO^-, SiOH, SiO^-) are responsible for lead removal, simply because GGBFS has more Si than Al, the silica surface sites should predominate. They are occupied by calcium and when GGBFS is placed in aqueous solutions both hydrolysis and ion exchange processes

begin. Under the experimental conditions used in this study, the surface calcium is changed by the hydrogen and lead and pH of 7.2. Kang et.al [2005] found that equilibrium adsorption of Pb decreases with pH, which may be associated with the change of electro kinetic potential of slag as a function of pH. It was found that the adsorption rate increases especially at lower initial concentrations of Pb2þ.

Zhang et al., [2007] have shown that GGBFS is a latent hydraulic material that can form C–S–H gel in the presence of a high pH as well as an alkali-activator. Consequently, GGBFS may be used as cement replacement. Zhang et al., [2007] and [Tsakiridis and Papadimitriou, 2008] also studied the use of Na_2SiO_3-activated GGBFS for solidification of municipal solid waste incinerator fly-ash. The compressive strength development and leachability of heavy metal contaminants were studied to evaluate the quality of the solidified waste. In addition, X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to examine the crystalline phases and the microstructures of the solidified municipal solid waste incinerator (MSWI) fly-ash.

1.4 Leaching

Leaching tests are applied to naturally contaminated or polluted soils tend to and be focused on ascertaining pollution levels and the mobility of those pollutants. Leaching tests are also used for determining: any deficiency of essential elements, possible toxicity and the physio-chemical behaviour of elements in soils. The information obtained is used for inventory and comparative purposes, and to decide questions such as possible counter-measures and land use. [Scanferla et al.,2009; Van der Sloot et al., 1997;Sanchez ,2003]

1.4.1 Leaching Test Objectives

Many batch leaching test protocols have been developed to simulate the leaching processes of waste materials in landfill or other disposal scenarios to evaluate potential risks to humans and/or groundwater systems [Timothy et al., 2003]. The results of batch leaching tests should be carefully Van der Sloot et al [1997] evaluated before being used for regulatory or design purposes have summarised the basic objectives of leaching tests as:
Classification of waste in terms of degree of the hazardous materials, and Evaluation of the potential of leaching pollutants, which will provide the specific leaching condition for simulation, and measure the efficiency of treatment of waste leaching with appropriate waste management scenarios in providing the actual amount of leaching represented in the

field. Standardisation is the procedure by which products specifications, performance requirements of processes and measurement methods are debated and operational limits defined. The final results of standardisation are laid down in standards, which are generally issued on a national basis, by bodies such as the BSI, or European CEN, or International ISO.[Van der Sloot et al 1997]With the growing importance of the leaching of waste from land and the need for re-use of construction materials, many countries, including those of the EU and the USA have developed and adopted tools to describe and identify types of leaching behaviour..

1.4.2 Extraction or Batch Type Tests

The performance of S/S-treated wastes is usually measured by leaching tests. Leaching is a method to remove soluble components from a solid matrix. A survey of the literature identified over 100 leaching methods [Kim et al., 2010] A number of different extraction or batch leaching procedures exist in which a certain amount of soil is brought into contact with a leachant, in a closed or open vessel and agitated for a certain period of time (normally to attain equilibrium/steady state conditions). The liquid and solid phases are subsequently separated and the liquid is analysed for the parameters of interest. Contact times typically vary from a few hours to a few days, and are often adjusted to accommodate normal working hours. In a single-batch leaching test, the procedure is performed once at a specified liquid to solid ratio (L/S). For most waste types, it is impractical to perform batch leaching tests at L/S ratios lower than approximately 2:1 l/kg.

The use of the same S/L (solid/liquid) ratio ensures that uniform comparison of results is obtained for the same material in different leaching experiments, as well as comparison of different leaching scenarios (e.g. landfill versus column). Secondly, assuming knowledge of hydrological conditions in any arbitrary scenario (e.g. landfill) allows the recalculation of the S/L ratio to leaching time.

Release of contaminants in the environment often occurs under conditions that are different from batch laboratory tests, because the release is affected by flow. However, the impact of flow on release can be simulated in batch leaching tests by conducting them at a range of L/S ratios. The laboratory results for a specific L/S can be applied to a flow system by considering a time period, over which the cumulative volume passing the waste gives the same L/S as the laboratory test [Batchelor, 2006].

The Tank Leaching Test for Compacted Granular Materials is a test in which the diffusion-driven leaching from compacted soil and waste materials is investigated. This test is mainly used for construction materials [BSI, 2004] but has recently been under assessment and consideration by the CEN/TC 292 [Horizontal EU project, 2003], to be used as a semi-dynamic test for characterisation of waste in soils. The results from the measurement of the release are related to the exposed surface area of the compacted waste; typically this test takes a long time to complete, lasting between 1-64 days. The description of tank tests by de Groot and Hoede [1994] and Townsend [2003] assumes diffusive leaching mechanisms and allows the determination of the effective diffusion coefficient, the cumulative release (mg/m^2) at 64 days and the diffusion coefficient (m^2/a).

Takahashi et al [2007] have shown that, as expected, the amount of leaching will increase with increase in L/S ratio. The leaching is a function of the surface area of the specimen and will depend on specimen shape, which is usually either cubic or cylindrical.

The concentration and pH influence the characteristics of the leachate. The main characteristics of the leachnat are the concentration of elements and the physical properties such as durability, freeze thaw and compressive strength of the final products. Pereira et al [2007] examined the effect of setting conditions (curing time, room temperature, etc) on leaching and the pH of the leachant and are in agreement with this statement.

However, Chaia et al [2009] have found that the effects of S/S appeared within the first week of curing, and believed that the reduction in leaching rate is mainly due to cementation. This is the same mechanism found with S/S used to treat contaminated land. Also the result implies that when using PFA and OPC as, say, embankment fill, providing a curing time of longer than one week, before opening the site to rain precipitation, can potentially reduce adverse environmental impact.

Shi and Fernandez [2006] have commented on the findings of Cho et al. [1999] who investigated the leachability of Pb^{2+} and Cr^{6+} immobilized in NaOH and sodium silicate-activated slag cement pastes. They noticed that the leachability of these two specific forms of lead and chromium in alkali-activated slag cement pastes did vary with curing conditions, but the variation was very small. They found a clear relationship between the diffusion coefficient of Cr^{6+} and the pore volume for those pores with a radius less than 5nm.

Ilić et al [2000] have noted that S/S in terms of the mixing of materials with binders and reagents, in order to reduce the leaching of contaminants, is a world-wide accepted treatment for immobilization of wastes such as heavy metals. The most commonly used medium in solidification/stabilization process is Portland cement, and pozzolanas such as fly ash from coal and solvent silicates.

Chrysochoo and Dermatas [2006] have shown that the stability domain for sulphate ettringite, reported in the literature, can lie in one of a number of different ranges of pH level occurring between 10.5 and 13. Myneni et al [1997] have claimed that the presence of ettringite may persist to a pH level as low as 9.5, dissolving partially to gypsum and $Al(OH)_3$. However, the most widely reported pH levels favourable for ettringite formation are between 11 and 12.5.

Qiao et al [2007] have found that metal aluminates, carbonate hydrates and calcium aluminate carbonate hydrates can be formed at the same time. This suggests possible new hydration products in which heavy metal cations have been substituted for Ca cations during hydration of C3A (tricalcium aluminate). Intermediate heavy metal aluminate hydrates produced after the addition of heavy metal hydroxides should be more metastable due to larger ion radii of these heavy metals and thus are easy to carbonate.

Liu et al [2005] have reported that the leaching of heavy metals from cement mortars is a diffusion controlled leaching process. Whereas leaching of Pb in pure water from mortar (e.g. OPC cube in water in a tank) seems to be a delayed diffusion controlled process
Numerous leaching tests can be used to assess S/S treatment, but no single test is able to fully describe the complex leaching behaviour of actual materials, and an accurate understanding of leaching mechanisms for proper interpretation of the different protocols. The most commonly used standard test is the toxicity characteristic leaching procedure, but this has the disadvantage of sometimes under-estimating the leachability of certain redox sensitive elements (e.g. As), because redox reactions may occur during extraction [Jing et al., 2004]. However, the number of tests available for determining leachability creates confusion as to which extraction test should be used in what circumstances, and how the results should be interpreted; for example, depending upon the purpose, the availability test (NEN 7341), the multiple extraction procedure and sequential chemical extraction can be applied to a wide range of materials. Van der Sloot et al [1996] proposed harmonization of the different leaching tests, but before this is possible there must be independent

verification of the consistency of results between the different test methods and for different types of wastes.

The presence of Pb contamination was found on 604 out of 1221 sites on the National Priorities List (NPL). Pb is the probably most common environmental contaminant and has chronic toxicity so there have been extensive studies of Pb immobilization in S/S-treated wastes.[Jing et al 2004].

Reviewing heavy metal immobilization in ettringite which is naturally formed in the OPC system ,C-S-H (using OPC), Gougaret et al., [1997] have reported that Pb can replace Ca^{2+} in the ettringite, but in the C-S-H structure Pb is immobilized by precipitation as carbonate and hydroxide. During cement hydration the stabilization of Pb in materials treated with cement is ascribed to the rapid precipitation of compounds of lead at the surface of colloidal materials. This precipitated layer of Pb acts as a diffusion barrier to water [Jing et al. 2004]. Van der Sloot et al.,2003;Sanchez et al., 2000] and many researchers [Jeong et al.,2005]have shown that the pH level of the leachate is the major factor in controlling the leaching of Pb. For neutral pH values of the leachant, low Pb concentrations are observed; when the pH level either increases to very high values or decreases to very low values Pb concentrations increase. Such amphoteric behaviour where the element appears to exhibit both metal and non-metal properties is due to solubilisation phenomenon at the solid-liquid interface (i.e., at the interface between the matrix and the leaching solution) [Johnson et al., 1996; Jing et al., 2004].

Leaching tests are conducted to examine mass transfer from a solid (the S/S material) to a liquid (termed the"leachant" before contact with the solid, and the "leachate" afterwards). Depending on the characteristics of the contaminated material and the surrounding environment, the leachant may flow through the contaminated material, maximising contact between the leachant and solid, and washout of contaminants, or flow around it, minimising contact between the leachant and solid, such that leaching occurs by diffusion of contaminants through the connected porosity of the sample. Hence the leachability (ability of the material to leach contaminants) is dependent on the physical and chemical properties of the contaminated material and the leachant. LaGrega et al., 1994;Perer et al., 2005].

Extraction tests are usually designed to reach a steady-state release, termed "equilibrium". Equilibrium-based leaching protocols typically require particle size reduction of the material under study, in order to reduce the time required to obtain steady-state release via increased surface area and minimized kinetic transport [Spence and Shi 2005]. Agitated extraction, shaking or stirring further accelerates the extraction rate and ensures continuous S/L contact. Common equilibrium tests are: single batch extraction, parallel batch extraction, sequential-batch extraction and concentration build-up extraction [Spence and Shi 2005].

Ososkov et al [1993] reported that no significant difference is detected in the extractive capabilities of the different mineral acids tested i.e, sulphuric, hydrochloric and nitric acids. An emphasis on temperature , concentration of acid, contact time and ratio of S/L effect on the extraction then stated that Sulphuric acid is a suitable choice as extractant because of its reduced cost and corrosively. Also Hamdy [2000] concluded that both NaOH and NH_4OH are unsuitable for metal elution compared with small amount of acids, HNO_3, HCl and H_2SO_4.Lai et al[2008] concluded that mixture of ($HNO_3/H_2SO_4/HCl$) with a volume ratio of 2:1:1 was better than (HNO_3/H_2SO_4 =1:1) to leach the metal.

Leaching behaviour of immobilised waste can be examined on cubic specimens of 5 cm side or slices of5 cm radius and 2 cm thickness with covered rim in>200 ml leachant. Conditioning of the specimens takes from one to a few days, depending on whether the surface is nozzle sprayed or exposed to an atmosphere saturated in water. Eventually, smaller specimens may be used to determine the specific density of the dry and completely wetted material and the effective porosity [DAS.1999]

The performance of the batch test

The leaching test was used in order to assess the success of the stabilization process. The batch test was conducted for a range of different conditions, before selecting the optimum conditions for the experiment to evaluate the removal of lead from the soil. The most important factors which have to be considered are the ratio of S/L, duration of contact between the solid and liquid (the leaching time or contact time), and the pH of the leaching fluid. A ratio of S/L of 1:10 was selected to follow the modified National Rivers Authority (NRA) test [NRA, 1994] for the U.K, which has superseded EN 14457-2. The NRA test

was considered as the preferred procedure because it is widely used in the UK and is relatively simple to perform.

After conducting many trial tests, it was decided that the optimum conditions for operating the batch shaking leaching test were an S/L ratio of 1:10 with DI water as the leaching fluid. The use of an S/L ratio of 1:10 and the conditions of operation such as the two hour contact time and the use of DI water, which were achievable in the laboratory facility, were comparable with the National River Authority Test (see Lewin, et al. [1994] and also the TLCP EPA test. The NRA test [Lewin, et al. 1994] used 100g of solid and 1000ml of deionised water, while the TLCP test used leaching fluid with controlled a pH of 5 with 18-24h leaching time and L/S ratio of 20. Thus the conditions of implementation of the leaching test here are close to those of the NRA test and can be described as a modified form of the NRA test. However, regardless of which test or tests are used, the leading regulatory agency should be involved in any project prior to investigation in contaminated soil as many aspects need to be considered in the leaching test [Testa, 1997].

1.5 Chemical analysis and spectroscopy techniques

The most used chemical analytical tools in this field are Fourier transform infrared (FTIR) analysis, Raman spectroscopy, X-ray diffraction (XRD), and X-ray photo spectroscopy (XPS). Table 1 .13 summarised the physical and chemical techniques used in this thesis to investigate processing of stabilization contaminated soils and solution

Table 1.13 Properties of techniques used to stabilize metal contaminated soils and solutions used in this study

Properties	Methods and techniques used	purpose
Batch Leaching test	shaking	extraction
Tank leaching test	NEN7345	extraction
Acid digestion test	HNO_3	extraction
Chemical concentration measurement	ICP, ion chromatography	Concentration, Metals , cations and an inions
Chemical bonds	FTIR , Raman	Chemical bond
Chemical structure and formation	XRD, FTIR, XPS Acid wash	Type of chemical compounds
Water content (%)	Oven, 105 ^{0} C	Water loss
strength	BS 196-1 and BS 1881-	Unconfined

NEN 7345 :Diffusion test. Tank test for monolithic wastes. Netherlands Normalisation Institute (NEN) .

1.5.1 Fourier transforms infrared spectroscopy (FTIR) and Raman spectroscopy

FTIR analysis was used to investigate bond relations, and to study the surface and interface chemistry of the cement-paste. FTIR absorption spectroscopy offers the advantages of identifying the polymorph as well as providing information on absorbed species [Ahmad and Collins, 1991]. FTIR spectrometers are cheaper than conventional spectrometers and provide the measurement of a single spectrum quicker because the information at all frequencies is collected simultaneously. Basil et al[2005] have used and reported that a FTIR system was developed to measure on-road emissions (CO_2, CO, NOx and 30 hydrocarbon species) in-vehicle using a portable FTIR. Chakraborty et al [2007] reported that Infrared spectroscopy can be used efficiently by polymer and rubber technologists for identification of polymer, polymer–blend ratio calculation, raw material evaluation, study of reaction mechanism, microstructure determination, etc.

FTIR spectroscopy has been the dominant technique used for measuring the infrared (IR) absorption and emission spectra of most materials, with substantial advantages in signal-to-noise ratio, resolution, speed and detection limits. The major advantage of the FTIR technique over other spectroscopic methods is that practically all compounds show characteristic absorption/emission in the IR spectral region and based on this property they can thus be analyzed both quantitatively and qualitatively. The quest for highly sensitive detection methods for atmospheric trace gas samples, either in laboratory setup or in outdoor remote sensing [Zoltn et al., 2004] .

However, in the Raman When monochromatic light (for example from a laser) is focused on a sample, some of it is transmitted, some is absorbed and some is scattered. Most of the scattered light will have the same wavelength as the incident light. However a small fraction of the scattered light - approximately 1 in 10^7 photons - is shifted in wavelength. This is because these molecules have experienced vibrations and rotations during the interaction with the light. The spectrum of this wavelength-shifted light is called the Raman spectrum. Raman spectra consist of sharp bands that are characteristic of the specific molecule in the sample. Each band of the spectrum corresponds to a specific vibration mode of the chemical bonds in the molecule [http://www.d3diagnostics.com/en/10371.aspx].However, the potential of Raman spectroscopy as an analytical technique for cementitious materials was first demonstrated by Newman et al [2005]. Potgieter-Vermaak et al [2006] considered the mineral cement phases alite (C3S), belite (C2S) and tricalcium aluminate (C3A) and found that the results

obtained with NIR FT–Raman and VIS Raman spectrometry were distinctly and consistently different for the calcium silicate phases.

Potgieter-Vermaak et al [2006] reported that carbonate was identified with all the lasers. The V1 and V4 vibrations of the carbonate were observed at 1084 and 712 cm^{-1}. However The use of Raman spectrometry on grey cements is reported not to be routinely successful and further investigation into the use of different lasers is advised Mestl et al [1993].

1.5.2 X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS)

XRD was used for identification of the crystalline mineral phases in the soil by Taube et al., [2008] and is widely used in the cement industry for quality control. The method is based on the calculation of X-ray diffraction patterns, and is a technique that characterizes the chemical structure of materials at the atomic level. XRD techniques, may offer particular advantages in identifying mineral forms that are related to structural parameters [Pattanaik, et al.,2004; Dongjin 2007].

X-ray Photoelectron Spectroscopy (XPS) is a quantitative spectroscopic technique that measures the elemental composition, empirical formula, chemical state and electronic state of the elements that exist within a materials The XPS uses to identify elements according to their binding and kinetic energies. In particular, XPS is widely used to investigate binding mechanisms of metal ions in cementitious materials because it allows relatively straight-forward analysis of the near-surface of materials. The technique utilizes soft X-rays which impinge on a surface, ejecting photoelectrons from valence and core levels of the surface and near-surface atoms. Thus XPS, by measuring the binding energy of electrons, allows elemental identification and provides chemical information about the oxidation state of the surface and near-surface atoms. Nevertheless, structural information gained from surface analysis techniques such as XPS is limited. For example, structural parameters of sorbing species such as bond lengths and the type of atoms adjacent to the sorbing species cannot be deduced [Scheidegger et al 2006; Haruhiko et al 1996].

XPS analysis it can offer significant micro-chemical information on material surfaces and is widely used [Hu et al, 2007]. Recent advances in XPS instrumentation have now made it possible to analyse small samples with improved spatial resolution and to make use of the so-called "imaging" XPS, where energies can be imaged with a spatial resolution of down to 3μm [James et al, 2008].

1.5.3 ESEM and SEM

The Environmental Scanning Electron Microscope (ESEM), Scanning Electron Microscope (SEM) and X-ray microanalysis (EDX) are used for qualitative analysis in stabilization technology. The BSE imaging is based on the spatial variation of the electron density and allows the optical identification of typical constituents of cement phases, based on grey level contrast and the morphology [Famy et al., 2002]. When BSE imaging is combined with energy dispersive EDX, spatially-resolved quantitative information of the chemical composition can be obtained. However, the (SEM) is used for surface and microstructure analysis, which it can be a vital part of the assessment of concrete and S/S technology.SEM uses electrons instead of light to scan a surface and can obtain information about the topography, including pore structure and composition. This technique can therefore provide valuable information about the microstructure of the concrete; can chemically map the surface, either generally or in 'spot' locations; as well as detecting inorganic contaminants such as salts and metals. From the SEM data, it is possible to assess the condition and composition of the concrete, Crofts [2006]. Many researchers (see, for example, Diamond [2004] and Rha et al [2000]) have concluded that no other technique can provide the same depth and breadth of information, in particular with use of the backscatter-mode, as ESEM.

1.5.4 X-ray Fluorescence Spectroscopy (XRF)

The XRF spectroscopy is widely used for the qualitative and quantitative elemental analysis of environmental, geological, biological, industrial and other samples. Compared to other competitive techniques. However, XRF has the advantage of being non-destructive, multi-elemental, fast and cost-effective. Furthermore, it provides a fairly uniform detection limit across a large portion of the Periodic Table and is applicable to a wide range of concentrations, from a 100% to few parts per million (ppm). Its main disadvantage is that analyses are generally restricted to elements heavier than fluorine.[Kalnicky and Singhvi, 2001].

1.5.5 Inductivity coupled Plasma –Atomic Emission Spectrometry (ICP-AES)

The Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) is one of the most common techniques for elemental analysis. Its high specificity, multi-element capability and good detection limits (ppm and ppb) result in the use of the technique in a large variety of applications. All kinds of dissolved samples can be analyzed, varying from

solutions containing high salt concentrations to diluted acids. A plasma source is used to dissociate the sample into its constituent atoms or ions, exciting them to a higher energy level. They return to their ground state by emitting photons of a characteristic wavelength depending on the element present. This light is recorded by an optical spectrometer. When calibrated against standards the technique provides a quantitative analysis of the original sample.

(ICP-AES) have been the EPA USA method of choice for the elemental analysis of soil extracts and aqueous samples because of their utility, sensitivity, and reliability. These methods can rapidly determine metals in trace amounts (after digestion) in many types of matrices. These methods are well-characterized and widely used, often for establishing analytical reference values for site samples [Steven and Nocerin 1995]. The ICP-AES was used in this study to measure the concentration of metals in the final solution after conducting the leaching test.

The principle of the ICP-AES is that a plasma source is used to make specific elements emit light, after which a spectrometer separates this light in the characteristic wavelength. A solid sample is normally first dissolved and mixed with water. The technique is robust enough to allow direct analysis of liquids. The sample solution is transformed into an aerosol by a nebuliser. The bigger droplets are separated from the smallest in a specially spray chamber. The smallest droplets (1-10 μm) are transferred by an argon flow into the heart of the ICP-AES, the argon the plasma. The bigger droplets (>90%) are pumped to waste. The function of plasma is to produce strong atomic emission from all chemical elements it is necessary to attain temperatures considerably above those available from simple flames. The highest amount of atomic emission is reached at temperatures in the range of 7,000 K to 10,000 K. In the ICP AES the solution required for analysis is usually 5 ml or lower and detection limits range from low parts per million to low parts per billion.

Solidification/stabilization (S/S) of hazardous waste is a widely used technology; therefore, it is crucial that its effectiveness can be evaluated and attempts made to improve the technique. There has been a large interest in studies dealing with leaching of stabilized metals such as arsenic, cadmium, chromium, and lead from cement waste forms. Immobilization by cement is effective for some metals and for some wastes, but not others. Since cement alone is not always effective, new and cheaper stabilizing agents are always sought for tailoring formulations when the need arises [Conner, 1990, Michael et al 2000]

The degree of effectiveness of these S/S products is defined basically by two parameters: strength and the leach resistance. The continuing need to develop economical and improved waste management techniques has increased the potential importance of solidification technology throughout the world, in a process defined as best demonstrated available technology (BDAT) [Malviya and Chaudhary 2006, Marija et al 2007].Methods used for studying effectiveness of S/S processes are physical, chemical and microstructural. Hills and Pollard [1997] used setting and strength development as indicators of solidification and the leach test to assess the extent of fixation. [Malviya and Chaudhary 2006], The long-term performance of S/S soils is closely linked to both the physical and chemical characteristics developed after binder addition and the exposure conditions in the field. To date, most studies relating to the S/S soils longevity are focused on understanding their chemical performance by applying a number of accelerated short-term leaching tests to synthetic S/S soils [Antemir A et al, 2010]

The toxicity characteristic leaching procedure (TCLP) is the current US-EPA standard protocol to evaluate metal leachability in wastes and contaminated soils. However, application of TCLP to assess Pb leachability from contaminated shooting range soils may be questionable [Cao and Dermatas. 2008]. In addition, many researchers have used only the leaching test and XRD or FTIR to study the mobilization of lead in soils or solution.

Dermatas et al. [2006] found that soil and Pb metallic fragment particle size plays a dominant role in the rate and amount of Pb release. They also found that Pb release was affected by soil pH, buffering capacity and mineralogy. Therefore it was required, in this study, to consider the particle size of soil and pH measurement. In addition to optimising the conditions of the batch test e.g. S/L ratio, duration, leaching fluid etc., the amount of binders used is varied to use blast furnace slag or fly ash to replace Portland cement, most of the previous studies used limited chemical equipment, e.g. XRD or FTIR , in addition to the leaching test.

The evaluation of S/S technology has not been fully investigated and understood, physical properties and long term stability of stabilized contaminated systems is still questionable Pirjo et al [1997] AlTabba [2005] in Star net (wwwstarnet.eng.cam.ac.uk/) confirmed that and indicated that S/S is accepted in the USA as an established treatment technology, however, its use in the UK has been limited to date. Further knowledge of the underlying

scientific and engineering principles and long-term performance will promote acceptance and widespread use of the technology

After achieving the stabilization and reducing the concentration of metals in solution and soils, it was required to perform further step, including the solidification status of the metals, also the type of compounds which would form as a result of adding and mixing the stabilizer to the contaminant. The limitation of using S/S are the curing time (setting time)greater than at least 7 days between the binders (cement or cement replaced with PFA or GGBFs), that will let S/S-treated materials usually have UCS performance standards starting at 50 psi [EPA US 2009].

In this study, another test was used to evaluate Pb and other metal leaching, by using and implementing a range of equipment to investigate the binding reaction between metals and stabilized material using the acid test, simple batch leaching test, tank leaching test, in addition to many chemical analytical techniques including: ICP, IC, FTIR, XRD, Raman, and XPS as well as measuring the unconfined compressive strength.

1.6 Aims and Objectives

The aims and the objectives of the research in this thesis are:

1. To investigate the nature of the binding between soil constituents and various pollutants, using different chemical analytical techniques including: XRD, FTIR, Raman, XPS and ESEM.
2. To determine the success of the stabilization process on by conducting leaching tests on representative samples.
3. To investigate the stabilisation of soil contaminated with pollutants, such as arsenic, cadmium, lead, mercury, zinc, etc., using a variety of blended binders, derived from industrial waste material such as fly-ash, slag, lime, and other materials.

Chapter Two

Material and methods

2.1 Introduction

This chapter explains the procedures which were taken to achieve the goals and objectives of this study. The main work was conducted on soils and stabiliser materials that were contaminated with lead and other metals in the laboratory. Also, work was performed on stabilization of contaminated soils and solutions with different methods and procedures. The final step was the solidification procedure which was implemented by using the tank leaching test. Chemical techniques were implemented to characterize the materials, such as ICPAES, IC, XRF, XRD, FTIR, RAMAN, XPS and ESEM as described below.

2.1.1 Safe working procedures

To prevent accidents, injury to persons and harm to the environment, strict Safe working practices were adopted in execution of the experimental procedures in this research. Prior to the commencement of every new set of experiments, a set of COSHH forms in which the chemical associate risks were assessed, were completed and discussed with the Department Safety Officer. Only after any recommendations had been incorporated and the procedures were approved was the experimental work commenced. The general procedures to ensure safe working are outlined below.

During sample preparation, gloves, a dust mask and a laboratory coat were worn. The waste materials from the sample preparation were carefully enclosed in plastic containers and handed over to the safety technician for disposal. Metal extraction using acids and other reagents was performed in a fume hood fitted with an automatic alarm system. Acid resistant gloves, laboratory coat and safety goggles were worn for personal protection. The extractants were carefully decanted into suitable containers within the confines of the fume hood. Waste materials were transferred to special containers for waste disposal, which when filled were safely disposed of by the relevant technical staff.

Strong acids and organic chemicals were stored in a separate reagent cupboards which were fitted with a fume extraction system. All acids and liquid chemicals were stored in Winchester bottles and were transported in Winchester bottle holders to prevent accidental spillage. All the analytical electrical equipment and instrumentation was university routinely checked by a qualified electrical safety technician. Routine maintenance of the instruments was carried out by suitably trained competent technical staff. All gas supplies were stored in a

well-ventilated, climate controlled alarmed storage room. The gas supply tubes were equipped with suitable valves and systems to turn off the supply in case of emergencies.

2.2 Remediation of lead contaminated soil

Figures 2.1, 2.2 and 2.3 show the flowcharts that summarize the experimental procedures which were carried out in this study, and explained in detail below.

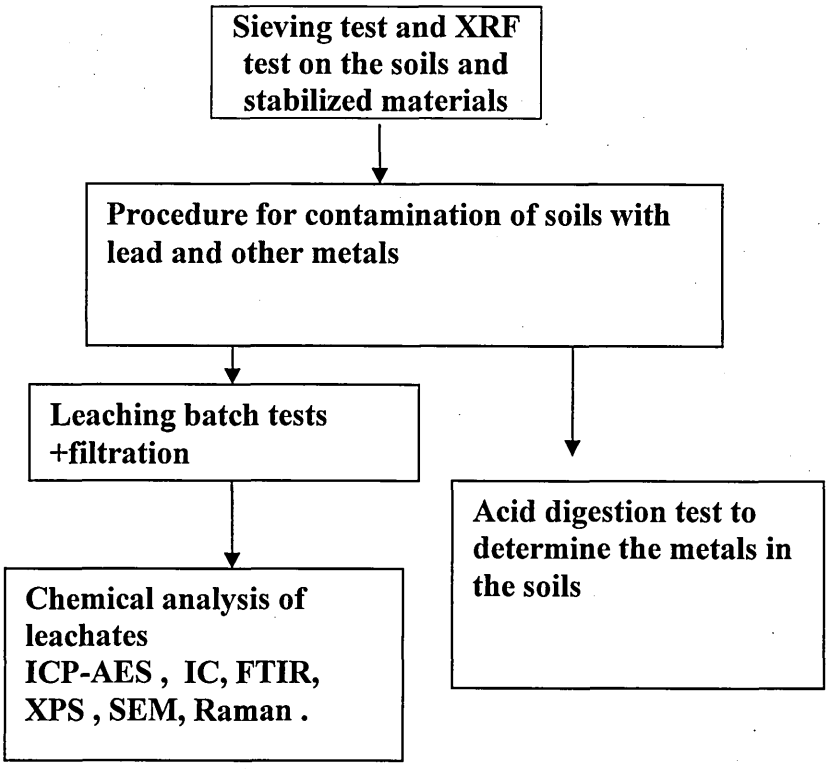

Figure 2.1 Flowchart showing experimental procedure for contamination of soils and subsequent analysis.

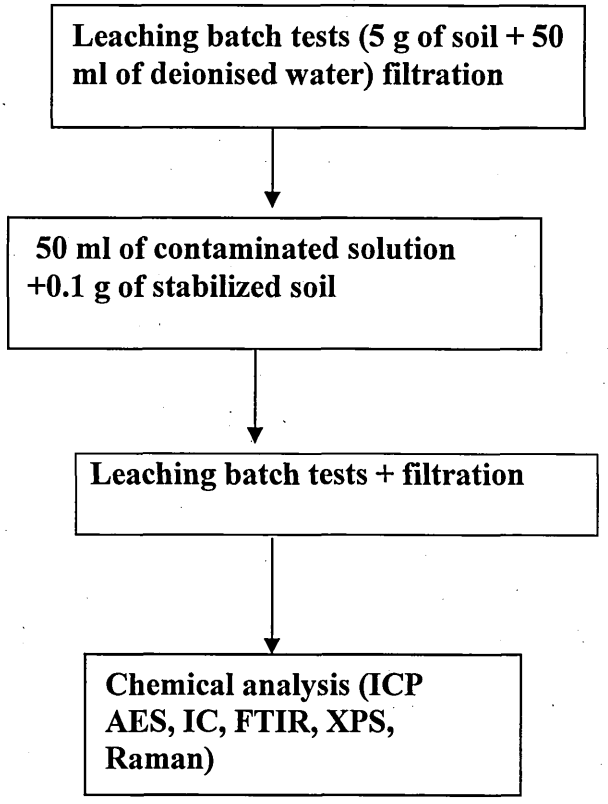

Figure 2.2 Flowchart for stabilization of contaminated solutions and subsequent analysis

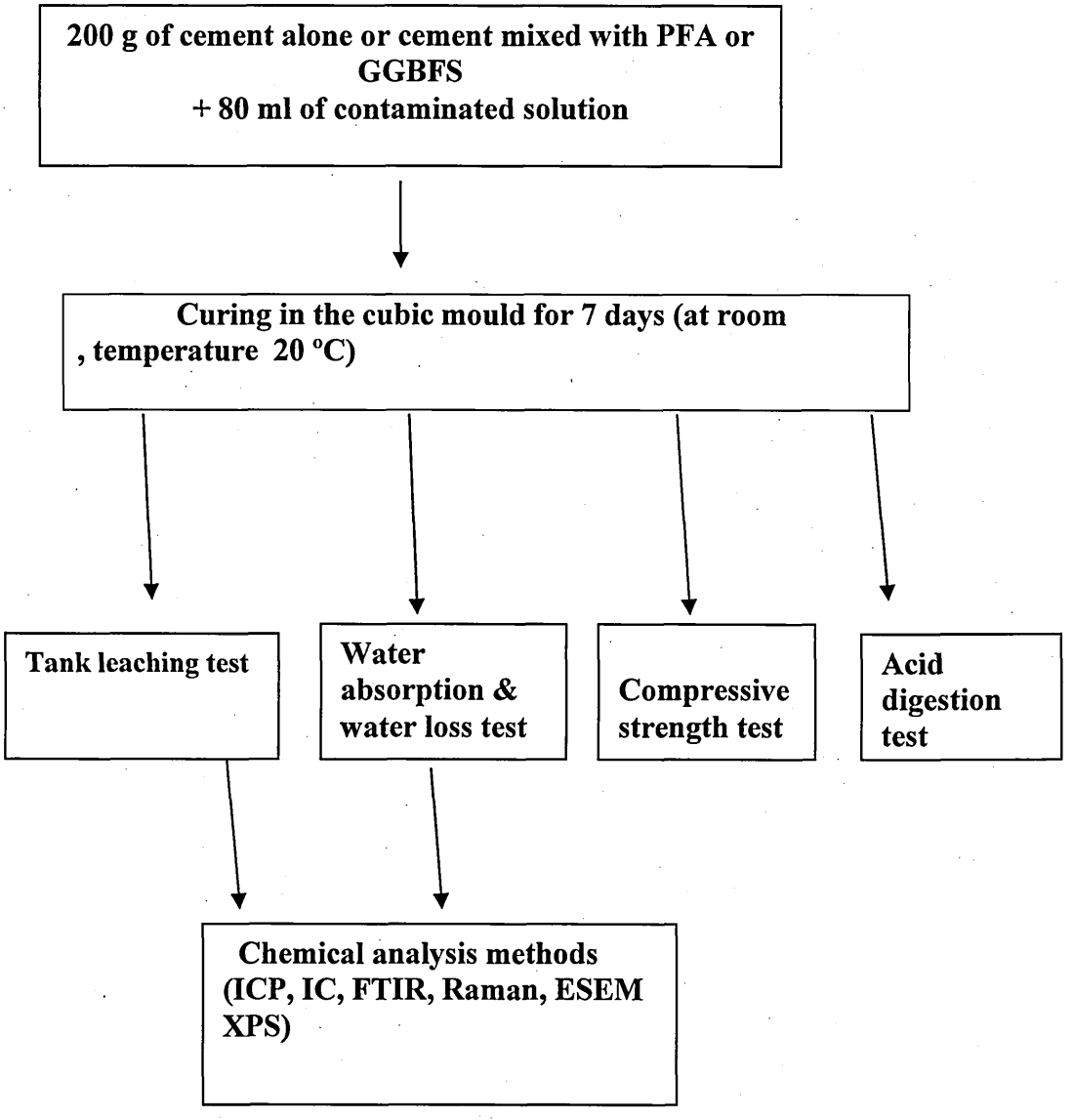

Figure 2.3 Flow chart diagram for solidification tests.

2.2.1 Characterisation of Soil Samples

Soil from Finningley Quarry in South Yorkshire, supplied by Lafarge Aggregates Ltd, was used for all the experiments reported in this thesis.

The soil was sieved according to BS 932-1/2 through a 5 mm sieve prior to the artificial contamination. The water content was determined by oven drying at 105 ^{0}C for 24 hours, as described in ASTM D 2216 2005.

Table 2.1 shows the properties of the uncontaminated and contaminated soils. The initial water content was 13.5 % before sieving. The soil composition shown in Table 2.2 was determined using XRF analysis, but Loss-on-ignition (LOI) was not determined. Sieved soils were used to prepare the contaminated soils, thus this difference of particle size between the contaminated and uncontaminated soils needs to be considered when the results of the tests are evaluated.

Table 2.1 Properties of the soils used in this study

Measured parameters	Uncontaminated soil	Contaminated soil
pH	6.9	5.7
Maximum particle diameter size	5mm	4mm
Water content % (w/w)	13.5 %	1.5 %
Lead in µg/g	ND (believed to be negligible)	172 µg/g

N D = None detected

Table 2 .2 Composition of uncontaminated soil used in this investigation determined by XRF

Compounds	Na_2O	Mg O	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	Ca O	TiO_2	Mn_3O_4	Fe_2O_3	Zn O	BaO
Concentration (% soil) (percentages of compounds shown sum to 99.5 %)	0.21	0.13	2.89	93.6	0.02	0.06	1.72	0.12	0.08	0.01	0.65	0.01	0.03

Nd=not detected =ZrO_2, Y_2O_3 , SrO , Cr_2O_3 , V_2O_5, LOI: not determined

2.2.2 Preparation of mixtures of metal solutions and reagents used in this study

Preliminary experiments were performed initially using Pb and subsequently a multi-element mixture was used. All the chemicals used in the study were of analytical reagent grade and the metals were added to the solution as nitrate salts. The amount of salt for each element was the amount required for a 1000mg/l concentration of the element in solution. For example 1.6g of $Pb(NO_3)_2$ was required to make 1000 mg/l of Pb solution and 4.93g of $Ni(NO_3)_2$ to prepare 1000 mg/l of Ni. Then individual masses for each element was dissolved into 1000 ml of deionised water and mixed thoroughly by shaking. Then 10ml of the mixed solution was taken and mixed with 100ml of deionised water to make 100mg/l of the metal solution. Final concentrations of the leaching solution were determined using ICP-AES to obtain a measurement of the composition of the solution See (Table 2.3) for the amount of each salts required to make 1000mg/l of metal solution also the chemical formula and the suppliers names, included the purity

Table 2.3 Salts used, mass required for solution strength of 1000mg/l

Chemical formula	Symbol	Mass in g for 1000mg/l	%Purity	Supplier
$Ni(NO_3)_2.6H_2O$	Ni	4.905	99	Merck
$Fe(NO_3)_3.9H_2O$	Fe	6.934	99	BDH
$AL(NO_3)_2.9H_2O$	Al	14.15	98.5	VWR
$Cr(NO_3)_3.9H_2O$	Cr	7.849	98	ALDRICH
$Cu(NO_3)_2.3H_2O$	Cu	3.802	99.5	Merck
$Cd(NO_3)_2.4H_2O$	Cd	2.799	98	ALDRICH
$Pb(NO_3)$	Pb	1.6		BDH
N2O6Zn.^H_2OZn	Zn	4.641	98	ALDRICH

2.2.3 Contamination Procedure

To artificially contaminate the soils in the laboratory, the equivalent of 1000 mg/l of Pb was added to 0.5 kg of soil in a 2 litre beaker, which then underwent constant shaking for 24h on a platform shaker at 300 rpm, by which time equilibrium was assumed to have been reached as assessed by experimental procedure described in chapter 3. The wet mix was then oven dried at 40^0C for 24 hours after which the dry soil was prepared for further investigation.

2.2.4 Acid Extraction test

The total leachable lead was obtained by digesting 1g of contaminated soil with average particle size of 600μm, achieved by sieving the raw soil prior to introducing the contaminant solution to the soil.

The digestion simple test was similar to the EPA US Method 3050, ICP-AES. The digestion acid test was conducted by placing 1g of contaminated soil, 5ml of HNO_3 and 20ml of DI water in a beaker on a hotplate and boiling for 10 minutes. The resulting solution was filtered and diluted with deionised water to a final volume of 25 ml. Similar procedures were followed to obtain the maximum extraction for soils contaminated with mixtures of metals.

A stabilized material such as OPC required only 0.1g of solid for digestion in 20ml of deionised water and 5ml of nitric acid. The same procedure was used to digest the soil. A vacuum was used to accelerate the filtration because some cement particles could not be dissolved, because of the gel composition of the cement. Whatman 542 ashless filter paper was used for soil samples.

Prior to use, the stabilized materials were tested to determine whether any contaminant could be found in the stabilized material. No detectable lead was found in the stabilized material except for lime, where a trace amount of lead (1.81 μg/g) was found. The investigation was carried out by using 25ml of leachant (20ml deionised water +5ml HNO_3 acid). The duration of the digester test 10 minutes boiled on hot plate.

An acid wash (0.001M HNO_3) was used on the filter and glassware after conducting the leaching tests. The concentration of lead in the wash solution increased, which demonstrates that lead was precipitated, and remained on the surface of the filter and the glassware. This is about same amount leached by deionised water. This helps answer the question of where the lead was precipitated since it was not detected using ICP-AES in the final solution from the leaching test.

2.2.5 Characterization of the stabilization materials

The feasibility study was used to investigate the chemical composition of contaminated and uncontaminated soils and the stabilized material using XRF quantity analysis, see Table 2.2

The pH values were also found for uncontaminated soil and for stabilized materials; the pH was determined at a ratio of 1:10 S/L. 5 g of solid (soil or binder material) and 50 ml of deionised water were shaken for two hours and filtered using 542 Whatman filter paper, then the pH of the elute was measured (Table 2.4). The uncontaminated soil had pH of 6.9, for OPC + uncontaminated soil the pH value was 12, for lime + uncontaminated soil the pH value was 6.7, for magnesia + uncontaminated soil the pH value was 10.3, for Fly ash +

uncontaminated soil the pH value was 8.7, and for GGBFs + uncontaminated soil the pH value was 10.2.

2.2.6 The apparatus for the Leaching batch test

A New Brunswick Innova 2000 Orbital Platform Shake supplied by Fisher UK, with Controlled Agitation from 25-500 rpm and adjustable time, was used to conduct the Batch leaching tests. The batch tests were conducted after achieving the optimum conditions. Different conditions and factors investigated were the ratio of liquid to solid L/S, duration of leaching, pH level and type of leaching fluid and speed of shaker for the mixing process. The solid / liquid ratio chosen was 1:10, which is the same ratio used in the National Rivers Authority (NRA) test and is equivalent to 5 g of solid to 50 ml of DI water or HNO_3. The speed of the platform shaker was kept constant at 300rpm for two hour duration (Innova2000 supplied by Fisher, New Brunswick Innova 2000 Orbital Platform Shaker). After conducting the batch leaching test, the leaching bottle (50 ml of solution in a 100 ml bottle) was transferred into a filter funnel and filtered through Whatman paper 542. The eluate (final solution) was kept until measurements by ICP were taken; the supernatant on the filter paper on the funnel were cleaned by acid wash until dissolved then measured by ICP (AES).

2.2.7 Inductivity coupled plasma (ICP-AES)

The ICP-AES was one of a number of analytical techniques used during the analytical procedures outlines in figures 2.1-2.3. The ICP spectrometer was an Activa supplied by Horbia Jobin Yvon, UK. The instrumental operation conditions are shown in Table 2.4.

Table 2.4 The conditions of the operation for ICP atomic emission spectroscopy (AES) in this project

Model	Spectra
spray chamber	cyclonic
Nebuliser	cross flow
Torch	Three piece
Sample introduction	Peristaltic pump
Gas	Argón
solution up take	0.8ml.min -1
Heating methods	Induction
No. of replicates	3
Power	1-2 kW
Rinsing time	20 s
Stabilization time	10 s
Transfer time	15 s
Normal speed of the pump	15 rate/min
Plasma gas flow rate	P(1/min)
Nebulisation flow rate	0.02(l/min)
Nebulisation pressure	1 bar
Elements	**Wavelength (nm)**
Lead	220.353
Cadmium	228.802
Zinc	213.856 and 206.191
Nickel	221.647
Copper	324.754
Chromium	283.563
Aluminium	309.271
Calcium	393.365
Magnesium	279.55
Sodium	588.99
Potassium	766.49
Iron	259.94

2.2.8 Ion chromatography ICS-90 system

The Dionex ICS-90 ion chromatograph system was used for analysis of cations and anions in the samples, the operation conditions are shown in Table 2.4.

The calibration solution was supplied by DIONEX, which contains seven compounds. The selected compounds in this project were chlorine, Cl^-, nitrate NO_3^- and sulphate SO_4^{2-}. The calibration standard solutions were 1, 10, 50 mg/l. The stock solution was supplied by Dionex at 1000 mg/l and was diluted to 100 mg/l and then this solution was further diluted to 50 mg/l and finally to the required working concentration of 1 mg/l. (see section 2.2.8 for description of calibration).

The main components of the IC-90 system include: Pump. Column, suppressor and injector. Operating conditions are detailed in Table 2.5. The system is controlled and data stored using the Chromelon SE software.

Table 2.5 Operation conditions for ion chromatography ICS-90 system

system	IC-90
The supplier	Dionex UK
Flow rate	2ml/min
Gas	N_2
Pressure	6 psi
elute	8 m M $NaCO_3$, 1.68 $NaHCO_3$ to 1000ml
diluted factor	20 times
regenerate	72 m N sulphuric acid
pump flow rate	0.2g/l
analysis time	10-15 min
conductivity	20-30 µs

2.2.9 Calibration measurement for IC (Ion Chromatography) and ICP (AES)

The 50 mg/l standard is a mixture of Cl^-, NO_3^- and SO_4^{2-}, and was used during the measurement by ion chromatography to check any drifting that may have occurred in the calibration.

Also the 10mg/l standard was used to check any drifting in calibration that may have occurred in the inductively coupled plasma calibration standard curves, during the measurement of metals concentration by ICP(AES). A matrix blank, analysed before the standard solutions, was used in all runs instead of a more typical 0.5% nitric acid blank. The reference material was of high purity (99.98 ± 0.02 % purity).

2.2.10 Fourier Transformation Infrared Spectroscopy (FTIR)

In order to study the precipitated materials it was necessary to establish the relationship between lead and the stabilizer materials. The assumption here is that there is a bond on the surface between the contaminated soils with lead and the stabilizer materials. The precipitate in the filter funnel was collected and FTIR used to investigate any bonds. FTIR offers the possibility of measuring different types of inter-atomic bond vibrations at different frequencies. The range of the FTIR is from about $2x10^{-6}$m to about $25x10^{-6}$m. FTIR was used to characterize the material after drying at 40^0C, as described below, and OMNICÔ software was used to collect the data. The procedure for conducting FTIR spectra analysis was as follows:

0.2g of dried Analar KBr powder was mixed with 0.0015g of the sample. Both materials were mixed and ground. The mixture was then pressed into a disk in a circular die with a diameter of 13mm, which was used to prepare the KBr disk. An argon atmosphere at 10Pa was used in the press to make the glassy disk.

The disk was placed on the disk holder and put into the IR spectrophotometer. Data were collected over 2-3 minutes and the spectrum of a blank KBr reference disk was subtracted.

2.2.11 Investigation by Environmental Electron Scanning Microscope (ESEM)

The Phillips ESEM 30XL and Phillips SEM 40 XL instruments were used in this study as follows.

The procedure for sample preparation for the ESEM Phillips XL30 was as follows: Carbon tabs were put on samples, which is as powder and then placed on 12mm aluminium tabs. The vacuum chamber was connected to nitrogen at a pressure of 10^{-6} Mpa. The electron beam was switched on and focused until the correct image was achieved, which then saved. The images were acquired using secondary electrons and ESEM images and EDX spectra for the area acquired. The area of interest was also mapped for various elements using the EDX and the associated software. Microscope control software was supplied by FEI-Philips.

The sample preparation for the SEM Phillips XL40 was as follows:

STUBS, 2 carbon tabs - the machine for carbon coating was the EMITECH K950x. This instrument was operated using a low-pressure argon atmosphere and the was connected to the machine for 5 minutes with the vacuum pump working.

2.2.12.1 X-ray Fluorescence spectroscopy (XRF)

XRF is a non-destructive, multi-elemental, fast and cost-effective method, applicable to a wide range of concentrations, from 100% to a few parts per million (ppm) and provides a fairly uniform detection limit for elements heavier than fluorine. XRF was used to analyse both the stabilized material and raw soil used in this research.

XRF analysis of composition of uncontaminated soil: contaminated soils and stabilized material were analysed during this work. The XRF instrument was a Philips2404 Magi X pro sequential spectrometer operating at 4 K with a tungsten sample holder, a vacuum pressure of 6 Pa and 30°C temperature, using the wide range oxides programme. The procedure for analysing the samples in this work was as follows:

Bead samples were fused with Di-lithium tetra-borate Anhydrous with a ratio 1:10, heated at 1200°C for 12 min, 1g of the unknown sample was mixed with 10g of lithium tetraborate $(Li_2BO_7)_2$: (this very light substance is recommended in the standard procedure) and placed in a furnace at 1200°C for 12 min. The sample was then put into a casting dish to form a fused bead. The sample was then measured on an oxide programme with Philips 2440 XRay fluorescence spectrometer. The major oxidised elements analysed are listed in table 2.2.

2.2.13 Raman spectroscopy Analysis

Whilst taking the measurements using Raman instrumentation it was considered in this study to increase the concentration of lead in the soils or as solution to 20,000mg/l in order to enable the Raman instrument to detect the lead in the samples.

Raman microscopy was carried out using the Renishaw RM1000 NIR system with a working range around 785 nm wavelength. The following parameters were used in order to collect data from the samples: x50 objective, 40 second scan time, 100% laser power.

Prior to analysis, the Raman instrument was calibrated using a silicon wafer; a spectrum of the silicon was collected in static mode with a 1 second scan time, using 100 % laser power. Grams software was used to collect the spectra.

2.2.14 X-ray Diffraction (XRD)

The XRD measurements were made according to the following procedure. The material was ground to a fine powder in a ball mill. 2g of the powdered material was weighed on a Denver microbalance and loaded into a standard sample holder. Powder XRD patterns were recorded at room temperature by a Philips X Pert diffractometer equipped with a diffracted beam monochromator and a scintillation detector using Cu Kα (k = 1.5406 A°) radiation. The data for all samples, including those of reference compounds, were collected in steps of 5 - 80 2theta with a counting time of 150 seconds per step, for total of 30 minutes. The international data base supplied by the Cambridge mineralogy database was used to identify the peaks of the spectra and the name of compounds.

2.2.15 XPS instrumentation

XPS measurements were made on a KRATOS AXIS 165 Ultra Photoelectron Spectrometer operated at 10 kV and 15 mA using the Al K(alpha) X-ray source (1486.6 eV). The takeoff angle was fixed at 90 degrees. The area corresponding to each acquisition was 400 μm in diameter. Each analysis consisted of a wide survey scan (pass energy 160eV, 1.0eV step size) and high-resolution scan (pass energy 20eV, 0.1eV step size) for Pb. The binding energies of the peaks were determined using the C 1s peak at 284.5 eV. The software Casa XPS 2.3.12 was used to fit the XPS spectra peaks.

2.3 Remediation of Lead Contaminated Solution

2.3.1 The contaminant of heavy metal

The lead was used as salts $Pb(NO_3)_2$ from BDH laboratory (Analar grade). Deionised water was obtained by using the deionised membrane apparatus. A Jenway pH meter was used to measure the pH of the solution; Whatman filter 542 Ashless was used for the filtration of the final solution of the heavy metals plus the stabilised material. The 0.2μm filter was used to collect the samples during the running of the tank leaching test.

2.3.2 pH measurement

The pH measurement was determined with Jenway350 pH meter for stabilised material in 0.1 g in 50 ml of deionised water. The sample was shaken for two hours and the elute measured after filtration by Whatman filter paper 542.

The pH meter was calibrated using buffer solutions (Aristar grad , BDH, UK) at pH value 4.0, 7.0 and 9.2 and the value of the soil solution were recorded and the electrode was washed with deionised water and immersed in the soil suspension. Three replicate reading of the suspension pH were taken. The calibration of the pH meter was rechecked against one of the buffer solutions prior to analysis of the next sample.

2.3.3 Preparation of the specimen and procedure of solidification

The weight of dry OPC was measured at about 200 g of OPC. The concentration of the metal solution was 20,000 mg/l, which was prepared in 1 litre and by dissolving the calculated amount of $PbNO_3$ (16 g per litre).

Prior to adding the optimum amount of the metals solution to the stabiliser materials, 6 M NaOH was added drop wise to adjust the pH to around 9. Then the metal sludge was mixed with cement using a plastic stirring rod before it was transferred into the plastic cube mould. This was left to set. This method ensured that 80 ml of metal solution and 200 g of ordinary Portland cement were mixed thoroughly using a plastic rod before being introduced to the plastic mould. The plastic mould and cubic specimen are shown in Figure. 2.4.

The samples were cured for 7 days at room temperature (20°C) before testing and immersion during the leaching tank test. For 20000mg/l*0.08 l, 16000mg of lead (i.e. 1.6 g) were present in each cube.

The relation for S/L was also measured as 1:5 and the leaching fluid was renewed each time. The design of the tank test with duration and interval numbers were in accordance with standard NEN7345 tank test. Table 2.7 and 2.6 explain the sampling procedure. The water was renewed when each sample was taken and samples were taken after 1 h, 2 h and 24 h and then at 24-h intervals until 120 hours

The replacement waste material GGBFS and PFA, were wet before the contaminated solution was introduced and the cubic specimen was placed in the plastic mould. Fig. 2.5 shows the specimen cube and the sample being suspended into the leaching fluid (deionised water). The optimum amount of replacement material (PFA or GGBFS) was added to the cement powder prior to adding any solution to the mixture of cement and any waste material.

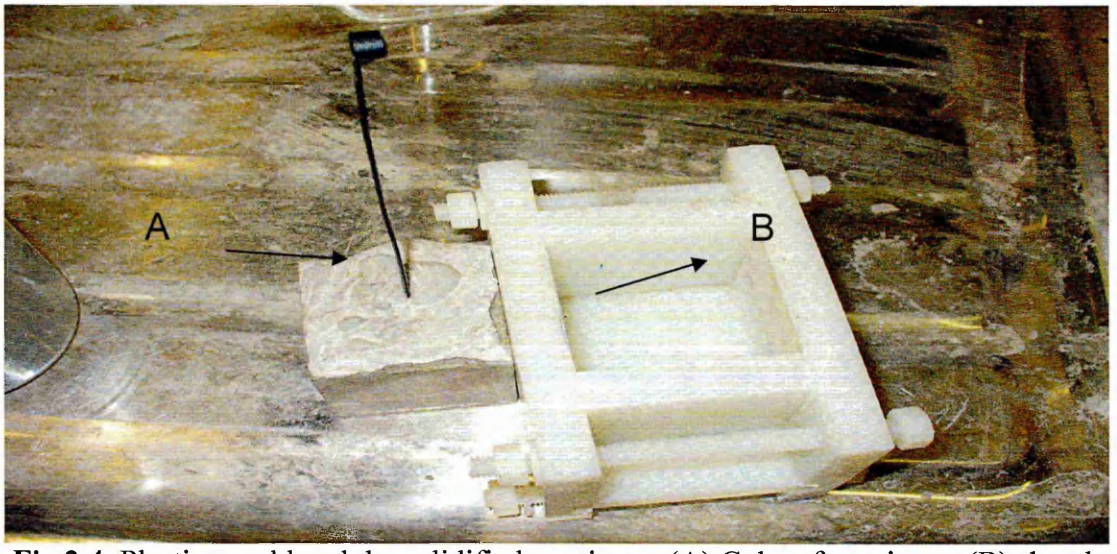

Fig.2.4 Plastic mould and the solidified specimen, (A) Cube of specimen, (B)-the plastic mould, 50x50x50mm

Table 2.6 Design and duration for the renewable tank leaching test and sample immersion

Specimen block	Total duration of immersion of OPC block in leachant (DI water) (hours)	Duration of leaching of each sample ,Time between samples) (hours)
1	*1*	*1*
2	*3(1+2)*	*2*
3	*27(24+3)*	*24*
4	*72(24+48)*	*48*
5	*120(48+72)*	*72*
6	*168(72+96)*	*96*
7	*216(96+120)*	*120*

2.3.4 Leachant refreshment in tank leaching test

Leachant refreshment: Prior to adding the pre-determined amount of metal solution to the stabilizing material a drop of 6 M NaOH was added to the solution to raise its pH to around 9. To accelerate the process of release from the OPC blocks, the leachant was replaced after each test period. That is, the tank was drained after 1 hour and the sample removed. The leachant was retained for analysis. Then the sample was replaced in the tank and the tank refilled with 625ml of DI water (+NaOH) to give a V/V ratio of 1:5. Then the tank was drained after a further 2 hours (total time of immersion of the OPC block, 3 hours) and the leachant again retained for analysis. The tank was refilled with leachant and the process repeated, and so on at time removal stated in Table 2.6.

Table 2.7 Description of tank leaching test

Shape of the specimen	The samples were concrete cubes of side 50mm (volume 125ml)
The leachant was DI water	
The ratio	The S/L ratio (V/V) was 1:5 so the volume of DI water inside the tank was 625 ml.
Leaching period	The leaching periods were fixed at 1, 2, 24, 48, 72, 96 and 120 hours
Temperature	The ambient (room) temperature was 20°C
Stirring	There was no stirring action during the tank test
No. of specimen	There were three block each in three separated tanks.
Measurement of the concentration of the samples	ICP-AES

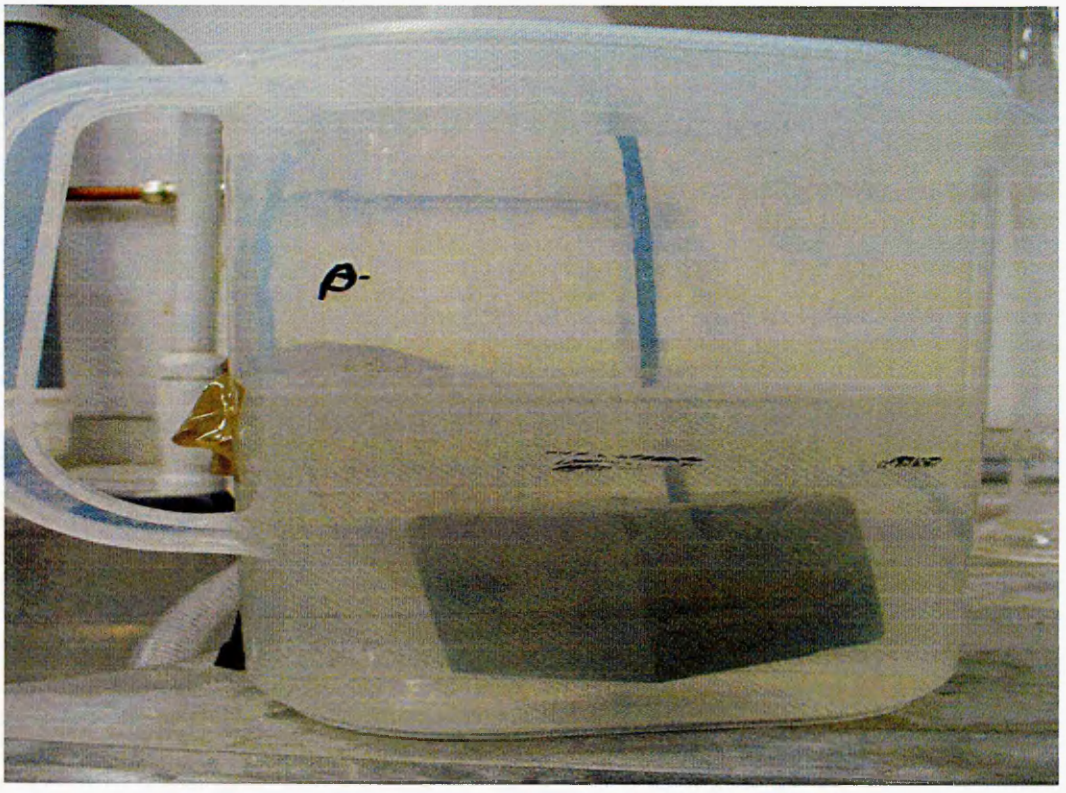

Figure 2.5 Tank test: 50mm OPC treated cube immersed in deionised water for tank test (1:5 S/L).

2.3.5 Unconfined Compressive strength (UCS) test

The compressive strength was measured by Universal Testing Machine (Model—TUN 400) described in Section 2.2.5. For UCS testing of unconfined compressive strength, 50mm cubes were prepared using different PFA/OPC ratios: 10%, 20% and 30% fly ash by total mass. The constituents were mixed dry before any fluid was added.

These were carried out with Avery DENSION machines based on a speed of 0.5, which measures the strength by KN. Figure 2.6 shows this equipment.

2.3.5.1 Strength Test

The unconfined strength of cubes was determined after 7 days and 28 days curing at room temperature (20 °C) and the values were compared with the design strength requirements for the concrete mix.

The load frame is a steel welded structure. It is designed to withstand a few million times of full cycles of loading without any sign of distortion or fatigue. These frames are light in weight. The base carries a fine finished hydraulic ram and the lower plate. The top plate has the spherical seating to take care of any irregularity of the specimen surface or slight misplacement of the specimen from the central position.

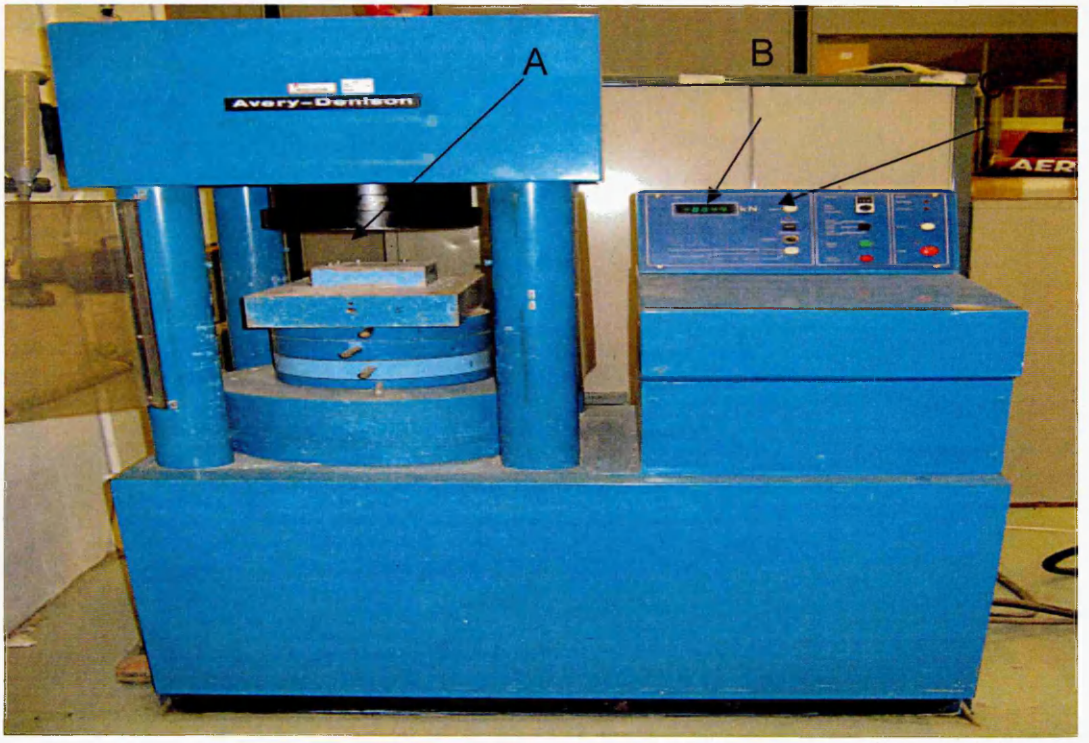

Figure 2.6 Compressive strength test equipment used to determined the strength of PC cube ,(A) Place of specimen, (B) Indicator of measuring .(C) Keys of operation.

Chapter Three

Effect of cement on metal contaminated soils and solutions

3.1 Background

This chapter describes the effect of OPC on contaminated soils and solutions. The subsequent results chapters (chapters 4-7), which report the effects of other stabilisers, are presented in a broadly similar way.

3.2 The Leachability of Lead

In this study the results of several leaching tests performed according to European Standard BS EN 12457-4:2002 *Characterization of waste*, on soil containing lead are compared and discussed. The test is described in the materials and methods chapter Two (2.2.4). Table 3.1 below presents the results for the mass of lead leached from the soil in μg/g. The mean amount of lead leached out is 781μg/g of soil. This represents the maximum extraction of lead from the soil and was achieved within 10 min heating on a hotplate using 5ml of HNO_3 and 20 ml of deionised (DI) water.

Table3.1. Results of the three total digestion tests for 1g of contaminated soil using a leaching solution 25ml (5ml acid+20ml water)

Sample	Concentration of lead extracted by leaching, (mg/l)	Mass of lead leached from soil, (μg/g)
Untreated Soil	31.3	782.5
Untreated Soil	32.7	817.5
Untreated Soil	29.7	742.5
Mean	31.2	780.8
Sd	1.5	37.5

Sd=standard deviation

The samples of raw, uncontaminated, soil referred to in Table 2.1 in chapter 2 were samples of urban soil. The water content in the contaminated soil was reduced to 1.5% by being dried in an oven. The lower pH of the contaminated soil was due to presence of the lead added to the soil. Also the particle size of the contaminated soils, was lower is due to the sieving process which was conducted prior to introducing the contamination solution. The soil properties of this soil are described in greater detail in Chapter 2 and Table 2.1.

Many researchers (including Uchida et al., 2005; Kara et al., 1997; Flavio, 2007) have adopted digestion test methods to determine the maximum availability of metals in soil. Kara et al. [1997] used the digestion test method to determine the total phosphorus in soil with 5 different reagents including Na_2CO_3 fusion, $HClO_4$, $HClO_4$ + HNO_3, HF + $HClO_4$ and NaOBr oxidation methods. Bingol and Akcay [2005] have used the digestion test to determine trace metals in fly ash using HCl as the solution, with different concentrations and combinations of HCl and HNO_3. Aqua regia (commonly 70% HNO_3 : 37% HCl = 1:3, v/v) is a strong acid leachant widely used to extract metals from solids. [Lai et al., 2008]. Our approach is similar to the EPA US Method 3050, using only 1 g of contaminated soils (see chapter two, 2.2.4).

The amount of lead released by acid digestion is greater than for the batch test extraction (Di water as leaching fluid) by a factor of 5 or more. During the experiments described there, the concentration of lead leached in the batch test was 34 μg/g by deionised water as leaching fluid and by acid digestion test was 781 μg/g (Table 3.1). This is because of heating of the sample, which accelerates the solubility and dissolution of lead in the sample. The other reason is using acid as a leaching fluid, at a temperature above room temperature. Simply the HNO_3 is a better extracting agent than water. However, the digestion acid test can estimate the amount of the metal bound in the particles of contaminated soil. In the presence of acid and a high temperature the lead will be dissolute and more soluble which causes a high release of lead and calcium.

3.3 Leaching test

3.3.1 S/L ratio optimisation

The objective of the laboratory trials was to perform the preliminary leaching test with different parameters – with emphasis on the length of leaching time, type of leaching fluid with different pH values (using different solutions of DI water and HNO_3) to examine different operational conditions - and identify appropriate conditions and select suitable parameters for the batch test. A S/L ratio of 1:10 and a constant vibration speed of 300 rpm for the platform shaker were used. Chaia et al. [2009] support the use of a S/L ratio of 1:10 for the batch test, leaching metal contaminated soil treated with cement. The different amounts of leachants that were extracted also depended on leaching time and type of fluid. The lead concentration was determined during each change in S/L ratio. Also the standard deviation was calculated for each ratio.

For soil contamination with lead, the calculation of release was based on 5 g of soil and various amounts of DI water (25 litres, 50, 100 and 200 ml) pH 5.6. Figure 3.1 shows the lead released with varying S/L ratios, from 1:5 to 1:40. Initially, increasing the value of S/L increases the amount of lead leached out but, interestingly, there appears to be an upper limit to the amount of lead released, in the region of 33 μg/g of lead in the leachate. Similar trends have been reported by others [see Karlfeldt et al, 1993; Halim et al, 2003; Veli, 2007; Erdem and Ozverdi, 2008].

The solubility equilibrium for any metal compound present is a limiting factor, which means that the S/L ratio needs to be optimized in order to get reproducible and reasonable results. The S/L ratio has an effect on other parameters in the leaching process. Here the concentration of lead in the leaching liquid increased as the S/L ratio was raised from 1:5 to 1:10. Over the range 1:10 to 1:40 the concentration of lead in the leaching fluid appeared constant at about 33μg/g; further increase of the S/L ratio led to a constant lead concentration a S/L ratio of 1:40 and above.

In this study, the average total leaching for all ratios is 115.9 μg/g. However at ratio1:5,the amount of leaching was equal to 9.7% of the total amount of lead, at a ratio 1:10, it was 32.5 %, at 1:20 ratio it was 27.7% and at 1:40 ratio it was 30% (see Fig.3.1 and Table 1 in appendix 1) .The leaching yields were calculated as mass of leaching / total leaching mass *100.

Starting with a low S/L, increased the leached amounts of lead. The result of this comparison was that the difference in leached amounts at L/S = 10 ranged over a factor of 4 between the highest and the lowest results. Similar results were reported by Fallman, et al.[1996].

Lead exists as Pb-hydroxy complexes under relatively highly alkaline conditions. In a previous study, when the S/L ratio was more than 1:20, and at higher than S/L 1:20 leaching of lead was attributed to the exposure of the waste to a higher absolute level of acidity, which was due to a low pH level of the leachant, thereby leading to a faster release of lead during the leaching period. The concentration of lead decreased because the pH decreased to values where lead was less soluble. Lower S/L-ratios led to a higher pH and by that a higher solubility of lead (Fallman et al. [1996]). Therefore, at S/L ratios of 1:10 and 1:20 the leachate pH was dominated by the alkalinity of the waste (Barna et al., 2005). Barna et al [2005] are in agreement with the results obtained in the current study and have

reported that at low S/L ratios, lead is more soluble mainly as a consequence of the pH and calcium evolution although in their study Ca release was not measured. The pH of leaching fluid in the work described in this section using deionised water as leachant was 5.6.

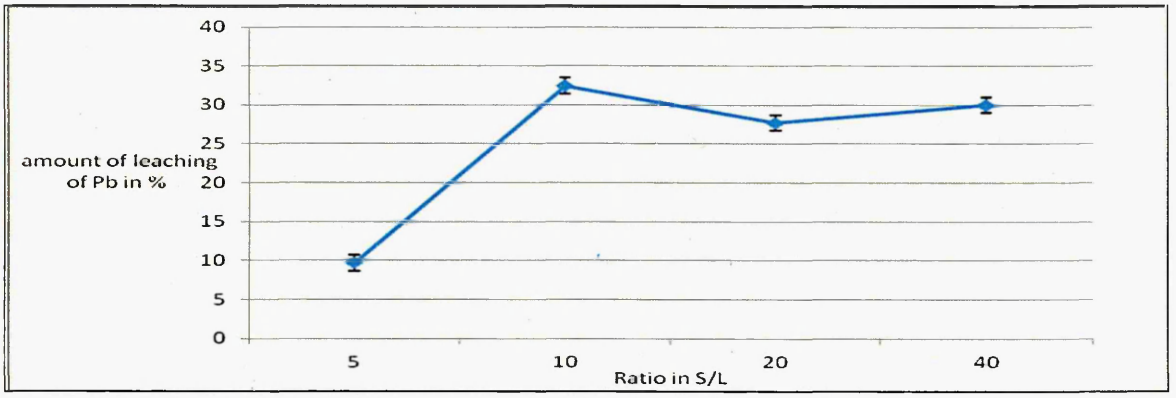

Figure 3.1 Effect of S/L ratio on percentage of leaching of Pb with using varied amounts of deionised water as leaching fluid (25, 50, 100, and 200 ml) (n=3) in this study.

Di Palma and Ferrantelli [2005] have reported that with an increase in the S/L ratio there was an increase in Cu and Ca leached from soils, which is a similar trend to that seen in this study, see Table 1 in appendix, which shows the effect of S/L ratio on amount of Pb leached out from contaminated soils. Di Palma also reported that an increase S/L ratio above 25 did not provide any further metal extraction. Feng et al. [2005] have also reported that the amounts of Pb and Zn leached out declined with a drop in the S/L ratio because of the dilution and neutralization processes that result in the decrease of pH value and the re-precipitation and co-precipitation of heavy metals, see Figure 3.2, adapted from Lai et al [2008]. In the study of Feng et al [2005], fly ash filed samples were used as specimen. Although in these experiments different amounts of soils were used with a constant volume of liquid, Jiang et al. [2009] have reported that the leaching concentration of Pb^{2+} increased with the increase of S/L ratio, which is in agreement with the results presented here. Two other studies (Bordas and Bourg, 2001; Idris and Hamid, 2008) have reported that at similar S/L ratios the release of metals initially increased with increase in S/L ratio and began to decline when the S/L ratio exceeded about 1:20. Moreover Bordas and Bourg [2001] reported that the S/L ratio had a strong effect on sorption of metals by solid (soil or sediment) and that the sorption increased with the S/L ratio.

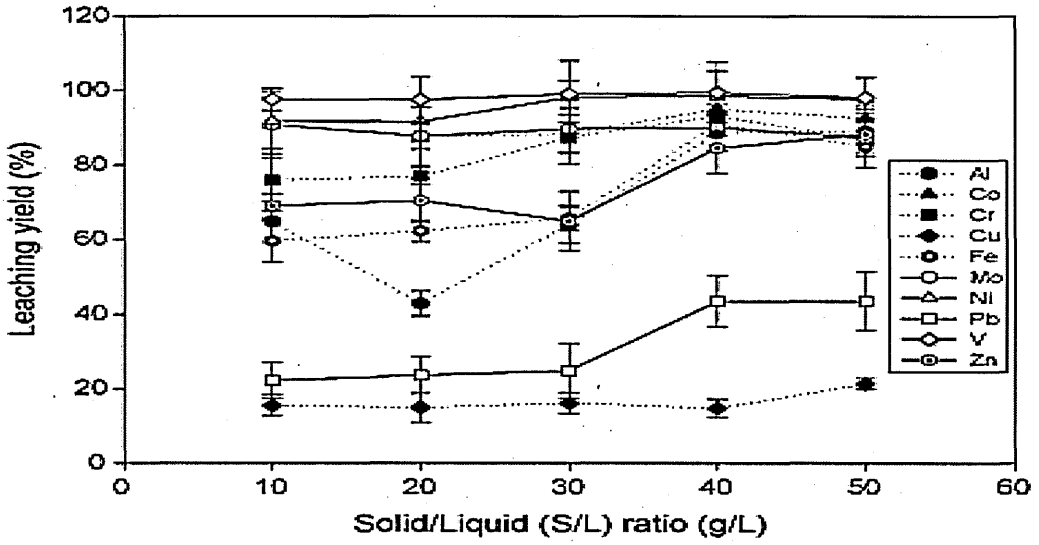

Figure 3.2 Effect of S/L ratio on metals leaching, adapted from Lai et al. [2008]

3.3.2 The effect of changes in pH of leaching fluid

The mean pH reading, and concentration of lead in the eluent, and their standard deviations are represented in Table 3.4, which shows the summary of finding in this study for the effect of pH of leaching fluid on leaching of lead contaminated soil. The release of lead from untreated, contaminated soil was 37.8 μg/g using DI water, pH 5.6, while with 0.01M HNO_3, pH 2.1 the result was 744μg/g. To better understand the cause of the different amounts released, another test was conducted using 0.1M HNO_3 solution at pH 1.1 and this increase the yield to 858 μg/g. The increase in the amount of lead released is attributed directly to the decrease in pH value. The effect of pH of the leachant fluid on the amount of lead removed has also been reported by Jing et al [2004] who examined the Toxicity Characteristic Leaching Procedure (TLCP) test using an extraction fluid with pH 5.1 and deionised water with pH 7.68. The latter value of pH 7.68 for the deionised water extraction was in the neutral to alkaline immobilization stage. In general, increased amounts of metal are released with decrease in the pH value. With increasing pH the metal solubility decreased to almost non-detectable levels which could be attributed to metal precipitation as hydroxides, as observed by Jing et al [2004] who also reported that the Pb concentration in the leachate of each test is mainly controlled by the leachate pH. Jing et al [2004] separated leaching behaviour into three stages which are: high alkalinity leaching stage at pH > 12, neutral to alkaline immobilization stage in the pH range of 6–12, and acid leaching stage with pH < 6, based on the leachate pH. The ion exchange occurred prior to participation of metals, in this study the pH of the rain water was 7.2, which is slightly basic. The effect of pH of the leaching fluid on release of lead from contaminated soil,

ratio 1:10 and duration of test 2 hour were found in this thesis for rain water pH value 7.2, and amount of leaching was 5.2 μg/g, with deionised water, pH value 5.6, the amount of leaching was 38 μg/g, with 0.01M HNO_3 pH value 2.2, the amount of leaching was 744 μg/g and 0.1M HNO_3 pH value 1.2 ,the amount of leaching was 858 μg/g.

3. 3.3 Effect of Contact Time

The investigation into the effect of the duration of leaching time was conducted by running the leaching test under the same conditions except for varying the time of contact between the leaching fluid and the contaminated soil. The release of lead was measured by ICP and the results are shown in Figure 3. 3 and Table 2 in appendix. It is important to run leaching tests with different contact times until equilibrium is reached and optimum conditions achieved. The aim of running the leaching test for different durations is to obtain an estimate of when the release of lead will have decreased to a sufficiently low level that it may be considered in equilibrium. This will give an estimate for the time by which any given proportion of the lead in the soil will have been released.

It can be seen that after the first 2 hours of contact, 34 μg/g of lead was released, and in the interval between 2 and 8 hours 37 μg/g was released. After 8 hours the rates of release of lead decreased sharply, and fell to a constant value, see Figure 3.3. This result is confirmed by the work of Karlfeldt and Steenari [2007] who obtained a similar trend with a leaching test with similar conditions using fly ash with water and acid. It must be borne in mind that Karfeldt and Steenari [2007] used fly ash, in which the lead was present primarily as $PbSO_4$ and $PbCO_3$ and it is possible that in the current study, where leaching from soil was investigated, the speciation of the lead may have been different (see section **3.5.5.3**). several hydroxides were in the leachant. Many metals show a low leachability due to formation of metal hydroxides within pH 9-11. Halim et al [2003] concluded that equilibrium in the release of lead with cementicious waste is reached after 18h, and drew attention to the adjustment of leaching time to 18 hour as the standard of test procedure AS 4439.3-1997 (Wastes, sediments and contaminated soils, Australian standard.) Again, Erdem and Ozverdi [2008] and Veli [2007] have reported that in the short term there is an increase in the leaching rate of Cr from soil, and Cu and Zn from clay, with increase in time, but after a certain duration the leaching rate falls. This current finding in relation to lead, in agreement with those reports. In terms of decreased of amount leaching after specific times, in this study an 8 h interval is the point of which leaching decreasing.

Figure 3.3 shows that the majority of the lead had been released after 8 hours contact. The cumulative extraction of lead was 91.3 µg/g (see mean and standard deviation in Table 2 in appendix 2). The percentage of release at 2 h were 36.8%, was 40 % at 8h with 37.2 µg/g , at 18 h were 7.5% with 6.9 µg/g, at 24 h were 5.5 % with 5.2 µg/g , at 48 h were 5.2 % with 5.2 µg/g, at 72h were 3.8 % with 3.8 µg/g. After 8 hours, the amount of leaching sharply decreased. Also Lai et al [2008] reported decreased leaching after one hour using acid as an extracting agent starting from zero hour to 0.5 h and 2 h.

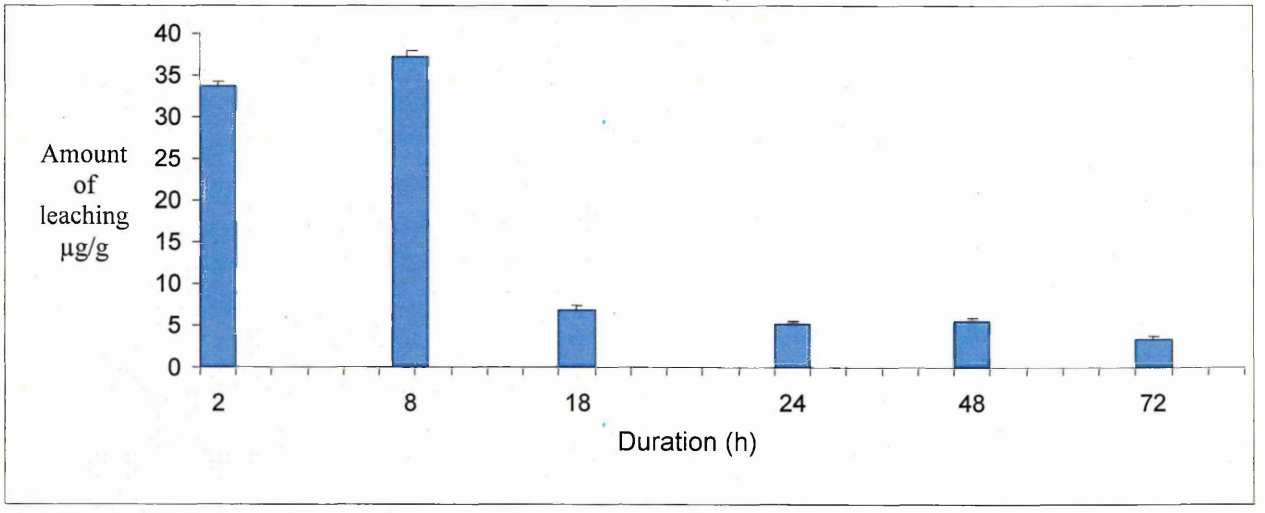

Figure 3.3 Effect of contact time on release of lead in batch test at S/L ratio of 1:10, 5g mass and 50 ml deionised water using 542 Whatman filter, speed rotary 300 rmp.(n=3)

3.4 Effect of OPC

From previous experiments carried out in this study the optimum conditions of operation for the batch leaching test were implemented for treating soils contaminated with lead solutions prior to investigating the effect of Ordinary Portland Cement (OPC) on soils contaminated with lead.

The four main minerals present in a Portland cement grain are: tricalcium silicate (Ca_3SiO_5), dicalcium silicate (Ca_2SiO_4), tricalcium aluminate ($Ca_3Al_2O_6$) and calcium aluminoferrite ($Ca_4Al_nFe_{2-n}O_7$). The formula of each of these minerals can be broken down into the basic calcium, silicon, aluminum and iron oxides see Table3.2. Cement chemists use abbreviated nomenclature based on oxides of various elements to indicate chemical

formulae of relevant species, i.e., C=CaO, S=SiO_2, A=Al_2O_3, and F=Fe_2O_3. The abbreviations for each oxide are as shown in Table 3.3 [Taylor, 1997].

Table 3.2 Chemical formulae and cement nomenclature for major constituents of Portland cement.

Mineral	Chemical Formula	Oxide Composition	Abbreviation
Tricalcium silicate (alite)	Ca_3SiO_5	$3CaO.SiO_2$	C3S
Dicalcium silicate (belite)	Ca_2SiO_4	$2CaO.SiO_2$	C2S
Tricalcium aluminate	$Ca_3Al_2O_6$	$3CaO.Al_2O_3$	C3A
Tetracalcium aluminoferrite	$Ca_4Al_nFe_{2-n}O_7$	$4CaO.Al_nFe_{2-n}O_3$	C4AF

Abbreviation notation: *C*=CaO, *S*=SiO2, *A*=Al2*O*3, *F*=Fe2

In this study the composition of the OPC was determined by XRF, the major constituents of the OPC used in the experiments are shown in Table 3.3, with CaO at nearly 63% being the dominant component. Lead nitrate was selected as the form of lead in the added contaminant solution because of its high solubility in water. The effects of metal nitrate salts on the microstructure development of OPC have been examined by a number researchers including Lina et al. [1996], Yukselen and Alpaslan [2001] and Al-Tabbaa and Perera [2002], who investigated the effects of metal and its concentration on cement hydration and porosity which has an impact on the microstructure development. Bednarsek [2007] has reported that immobilization of some types of contaminants was achieved by direct reaction between the contaminants and the OPC. Testa [1997] found that metal ions are chemically immobilised by pH-controlled precipitation, by incorporation into crystalline hydrates, or by precipitation as hydrated metal silicates, hydroxides and oxides.

Table 3.3 XRF analysis for the chemical composition (by mass %) for OPC and uncontaminated soil used in this study

Compound	pH	SiO_2	Fe_2O_3	Al_2O_3	TiO_2	CaO	MgO	SO_3	K_2O	Na_2O	Mn_3O_4
OPC	12.3 (0.1g of OPC in 50ml of DI water)	19.3	2.3	4.9	0.5	62.8	0.9	0.4	0.5	0.4	2.3
Uncontaminated Soil (5g)	6.9 Soil solution	93.6	0.7	2.9	0.1	0.1	0.1	0.1	1.7	0.2	0.0

Mass of soil=5g , LOI= not determined

The effect on the lead solution of adjusting the pH of the contaminated solution by the addition of NaOH, were examined, see Table 3 in appendices. The addition of a 1 μL solution of NaOH of 2 M changed the pH value of the leachant from 2.2 to 6.9. Full

mobilisation was reached at a pH level of 5.45. The addition of hydrated lime and OPC to the lead solution increased the pH and successful mobilisation of metals to the surface was obtained. The pulverised fly ash (PFA) did not sufficiently increase the pH of the contaminated solution and therefore did not mobilize the lead in the solution. The mobilization occurred only with addition of NaOH which consequently increased the pH.

In the experimental work undertaken in this study shows the effect of increasing the pH of the leachant on the concentration of lead in the leachant was determined. It can be observed that the lead concentration remained low until the pH increased above 5.5. The lead solution has pH value 2.5 and adding PFA to the solution did not increase the final pH after shaking for 2 hours and filtering through 542 Whatman filter paper. After adding NaOH to 10 mg/l of lead solution and 0.1 g of PFA, a decrease in lead concentration in the final leaching solution, at pH 6.2, was seen. The concentration of lead was reduced to 0.2 mg/l from 10 mg/l, see Table 3 in Appendices.

Adding 0.1g of OPC to the lead solution resulted in the reduction in the concentration of lead in solution by 99% of the total concentration. During the process of adding OPC to the lead solution it was noticed that an amount of OPC remained in the bottom of the beaker and also increased the pH in the final solution. This observation gives indication to the usefulness of cement the indication being mainly on alkalinity properties of cement as a binding and stabilising material with a solidifying agent represented by CaO, and Si.

The pH of the uncontaminated soil was 6.9, The effect of adding 0.1g OPC to 50 ml of DI water increased the pH value to between 12 and 12.7, and with it the increased release of calcium, potassium and sodium, see Table 3.7. The pH of the contaminated soil was 5.4. the lead solution was added to uncontaminated soil and dried (see chapter two material and methods contamination procedure). The pH of contaminated soil was lower than uncontaminated soil because of lead associated to soil caused an increase of the pH to 4-5, (see Table 3. 4), and this rose to 12.2 with the addition of the OPC. The procedure for adding the stabilizing material was to mix the dry bases; 0.1g of OPC with 5 gram of contaminated soil, and then introduce 50 ml of the leaching fluid. The batch test with DI water shows a decrease of leached lead from soils treated with OPC stabilising material, see Table 3. 4.

Table 3.4 Effect of stabilizing material on release of lead with various leaching fluids

Leaching fluid	Sample	pH	Pb (µg/g)	Ca (µg/g)	Mg (µg/g)	Na (µg/g)	K (µg/g)
De-ionised water	contaminated soil	5.4	37.6	180	19	5.4	17
	0.1 g of OPC+ contaminated soil	12.2	0	2192	0	14	80
0.01MHNO_3	contaminated soil	2.2	744	2400	270	4	19.6
	0.1g of OPC+ contaminated soil	11.9	2.6	19900	0	25	85
0.1MHNO_3	contaminated soil	1.2	858	2600	280	5	22.1
	0.1g of OPC+ contaminated soil	1.2	597	44900	403	37	102

From Table 3.4 it can be seen that high release for all the elements was obtained using leaching fluid with high acidity, 0.1MHNO_3, pH 1.2.

In this study it was found that there was a large increase (2,200 µg/g) in release of Ca with the addition of the OPC to the leaching process, see Tables 3.6 and 3.7. This is due to the presence of CaO in the cement. In addition there was increased release of Al, K, and Na with the addition of OPC. The amounts of Na and K released were 14.5 µg/g and 79.7 µg/g, respectively from OPC-treated soil, while in the absence of OPC the corresponding concentrations were 0.13 µg/g and 17 µg/g respectively. This difference can be attributed to the increase in pH value due to OPC. In this study, also increased release amounts of anions about half amount of chlorine to18 µg/g from untreated soils was 9.5 µg/g and 617 µg/g in sulphate from only 25 µg/g in non treated samples. However Scanning Electron Microscope (SEM) results confirmed that lead was coating the cement particles; see Section 3.5.4, especially Figure 3.11.

Thevanin and Pera [1999] have studied the interactions between lead and OPC. They concluded that lead stabilisation in hydraulic binders occurs due to a combination of the following mechanisms:

Addition: C-S-H + Pb→Pb-C-S-H.

Substitution: C-S-H + Pb→Pb-S-H + calcium.

Precipitation of new compounds: $Pb + OH^- + Ca^{2+} + SO_4^{2-} \rightarrow$ mixed salts.

Where C-S-H is calcium silicate hydrate.

Portlandite ($Ca(OH)_2$) and C–S–H are the main minerals produced by the hydration of cement. Dongjin [2007] showed that cement–water systems generate significant quantities of calcium–silicate–hydrate (C–S–H) within a few days of hydration. The C–S–H, which has a high specific surface area with its high density of irregular hydrogen bonding, creates a strong potential for sorption. In areas, external to the C–S–H, there are chemical reactions such as chemisorptions, substitution, ion exchange and adsorption among cement pore–water components and organic/inorganic contaminants. Dongjin [2007].

Table 3.5 Effect of OPC on concentration of lead leached from contaminated soils using 50ml of de-ionised water

Sample	pH	Pb (µg/g)	Si (µg/g)	Mg (µg/g)	Al (µg/g)	Ca (µg/g)	Na (µg/g)	K (µg/g)	Cl^- (µg/g)	NO_3^- (µg/g)	SO_4^{2-} (µg/g)
Contaminated soil	5.0	34	N/D	22.3	0.95	140.7	N/D	13	16.7	613	15.3
Contaminated soil	5.5	34	N/D	17.1	N/D	136.8	N/D	17.2	5.5	582	22.1
Contaminated soil	5.7	39	N/D	15.3	N/D	129.9	N/D	23	9.3	865	24.7
Contaminated soil	5.5	50	N/D	22.5	N/D	164.5	0.132	16.8	6.2	865	41.9
Mean	5.4	39		19.3		142.9		17.5	9.4	731	25.9
Sd	0.36	2.8		3.6		5.4		5	5.6	155	4.8
5g Contaminated soil + 0.1g OPC	12.0	N/D	20.6	N/D	3.26	1471.4	13.3	87.6	12.1	618	388
5g Contaminated soil+ 0.1g OPC	12.0	N/D	32.5	N/D	4.36	2414.5	11	73	33.7	492	393
5g Contaminated soil + 0.1g OPC	12.0	N/D	30.8	N/D	4.74	2692.9	18.7	78.6	8.3	597	1071
Mean	12		27.9		4.12	2192	14.3	79.7	18.0	569	617
Sd	0		6.4		0.7	640	3.9	7.3	13.7	67.5	392
Uncontaminated soil	6.9	N/D	N/D	N/D	N/D	N/D	N/D	N/D	5.1	128	7.7
Uncontaminated soil	6.5	N/D	N/D	N/D	N/D	N/D	N/D	N/D	6.0	132	11.3
Uncontaminated soil	6.4	N/D	N/D	N/D	N/D	N/D	N/D	N/D	5.5	121	9.6
Mean	6.6								5.5	127	9.5
Sd	0.24								0.4	5.3	1.7

N/D: below detection limit of ICP (AES) and negative value

To conclude, 0.1g of OPC, which was 2% of the total mass of solid soil sample, was sufficient to immobilise the lead in the soil by almost 99%. Alpaslan and Yukselen [2002] have effectively immobilised lead by 99 % using a ratio of cement to soil of 1:15. Their leaching test was on urban contaminated soil composed of 19% sand, 20% clay, 56% silt with a total lead content of 600 mg/kg. Jing et al [2004], used 10 % of OPC to treat lead

contaminated soil . In this study only 1:50 (0.1g: 5 g), cement to lead contaminated soils ratio were used to immobilise 99% of Pb.

3.4.1 The effect of OPC on lead in solution

The effect of OPC on different concentrations of lead in solution, 10, 100, 500 and 1000mg/l, was investigated; see Tables 3.6, 3.7 and 3. 8. The lead solution was thoroughly mixed with 0.1g of OPC and shaken for two hours and filtered with 542 Whatman paper, the supernatant was collected to allow the use of other techniques to investigate the presence of lead compound in the OPC. The pH values in the eluted solution were increased to 12, which is compatible with high release of calcium and removal of Pb. The levels of NO_3^- shown in Table 3.7 were the highest 1114 μg/g because of the high solubility of $Pb(NO_3)_2$, followed by sulphate 69 mg/l and chlorine 1.1 mg/l.

The pH is a determining parameter for the control of heavy metal mobility in aqueous solutions. Adding NaOH to a metal solution will increase the pH, which means the alkalinity will affect the state of the metals, see Table 3 in appendix. Mixing OPC with a metal solution, shaking it for two hours then filtering with 542 Whatman filter paper resulted in a 99% reduction of concentration of lead in solution, see Table 3.7. [Mari and Hamlin 2001; Jian-feng et al 2009 and Gundersen and Steinnes 2003] have observed similar effects of increased pH on the mobility of heavy metals. In Table 3.7 the concentration were measured after adding the OPC powder and shaking for two hours then filtered with Whatman filter paper 542.

Table 3. 6 Effect on pH level of 0.1g of OPC in lead solution

Sample	Conc. of Pb in final solution (mg/l)	Mean Conc. of lead (mg/)l	Sd	pH
500 mg/l of Pb + 0.1g OPC	0.2			11.7
500 mg/l of Pb + 0.1g OPC	0.2	**0.2**	**0.0**	11.3
500 mg/l of Pb + 0.1g OPC	0.2			11.7
Acid wash				
0.1g of OPC (filter andglass)	378			
0.1g of OPC (glass)	160			
0.1g of OPC (glass)	234			

Table 3.7 Effect of 0.1g of OPC on a solution of Pb (1000 mg/l) and amounts of compounds of Cl^-, NO_3^-, and SO_4^{2-} released as a consequence in leaching fluid

Sample	Pb (mg/l)	Mg (mg/l)	Ca (mg/l)	Na (mg/l)	K (mg/l)	Cl^- (mg/l)	NO_3^- (mg/l)	SO_4^{2-} (mg/l)
0.1g OPC + 1000 mg/l Pb solution	2.3	3.12	1488	10.8	35	1.2	1427	69
0.1g OPC + 1000 mg/l Pb solution	9.2	0.76	806	7.36	33.6	0.9	927	54
0.1g OPC + 1000 mg/l Pb solution	1.1	0.64	1244	12.1	56.5	1.1	988	168
Mean	4.3	4.2	1179	10.1	41.7	1.1	1114	97
Sd	4.3	1.4	345	2.5	12.8	0.2	354	62

3.4.2 The effect of OPC on soil contaminated with Pb, Cd, Cr, Cu, Ni and Zn

Table 3. 8 shows the effect of the addition of OPC to contaminated soil which contained a 1000 mg/l solution of a mixture of heavy metals (Pb, Zn, Ni, Cd, Cr, Cu) in DI water, see Chapter Two, section 2.24, on material and methods, for details of the contamination process. The leaching batch tests were conducted for 2 hours on the platform shaker. The S/L ratio was 1:10 and the leaching fluid was 50ml of DI water. The treated soils had a pH of 11.9 and the concentration of lead was almost undetectable. The average release of SO_4^{2-} was 971µg/g, of Cl^- was 11.4µg/g and the highest release was for NO_3, over 11,000 µg/g. The initial values were 15.5 µg/g for Cl^-, 11710 µg/g for NO_3^-, 28.1µg/g for SO_4^{2-}. See Table 3.5 for uncontaminated soils. Table 3.8 clearly shows that OPC has reduced the leaching of metals in contaminated soils to below the limit of detection of the measurement techniques which is negative value.

The average concentrations released from the contaminated soil, leached out with DI water, were 884ug/g for Pb, 905 µg/g for Cr, 964 µg/g for Zn, 1005 µg/g for Cu, and the highest recorded value was for Cd at 1079 µg/g. The lead released in the presence of other contaminating metals was higher than when it was on its own, 884 µg/g compared to 39 µg/g. The average releases of the anions were 15.1µg/g for Cl^-, 281ug/g for SO_4^{2-} and 11710 µg/g for NO_3^-. The large amount of NO_3^- released was due to presence of lead nitrate used to contaminate the soil. For soil treated with OPC the release of SO_4^{2-} from treated soil was higher due to presence of SO_4^{2-} in the cement composition.

Table 3.8 The effect of OPC on release of mixtures of heavy metals (Pb, Cd, Cr, Cu, Ni and Zn) from contaminated soils, leached with 50 ml of deionised water

Sample	Pb (µg/g)	Zn (µg/g)	Ni (µg/g)	Cd (µg/g)	Cr (µg/g)	Cu (µg/g)	pH	Cl^- (µg/g)	NO_3^- (µg/g)	SO_4^{2-} (µg/g)
contaminated soil mix	857	880	905	987	881	927	4.05	17.1	18890	20.7
contaminated soil mix	883	1065	1084	1193	902	1107	3.97	17.0	18750	33.7
contaminated soil mix	912	946	975	1056	933	980	3.87	11.2	16370	30.0
Mean	884	964	988	1079	905	1005	3.9	15.1	18003.2	28.1
Sd	27.6	93.7	90.2	104.9	26.2	92.5	0.1			
contaminated soil mixture +OPC	N/D	N/D	N/D	N/D	N/D	N/D	11.7	8.4	14959	865
contaminated soil mixture +OPC	N/D	N/D	N/D	N/D	N/D	N/D	12.0	15.3	8229	856
contaminated soil mixture +OPC	N/D	N/D	N/D	N/D	N/D	N/D	11.9	10.6	10336	1192
Mean							11.9	11.4	11175	971
Sd							0.1	3.6	3442	192

ND=none detect: negative value

The leachate samples were digested using a hotplate acid digestion procedure similar to that applied by Townsend et al., [2008]. The maximum extractions of Pb, Cd, Cr, Cu, Ni and Zn obtained for 1g of contaminated soil using the total digestion acid test with 5ml of HNO_3 and 25ml of deionised water on a hotplate for 10 min, and filtered with Whatman 543 ashless filters are shown in Figure 3.4. The results of the digestion test do depend on type of leaching fluid being used and duration of the heating of the samples and also whether the extraction was single or multi stage. Boardman [1998] used both HNO_3, and H_2SO_4 with two step extraction and reported greater extraction in the two steps methods although after first step the greater amount of metal leached out. The mean of the maximum extraction amounts were as follows Zn 1212.2 µg/g, Cd, 987.8 µg/g, Pb ,915.2, µg/g Ni , 503.3 µg/g, Cr, 485.9 µg/g and Cu, 440.3 µg/g.

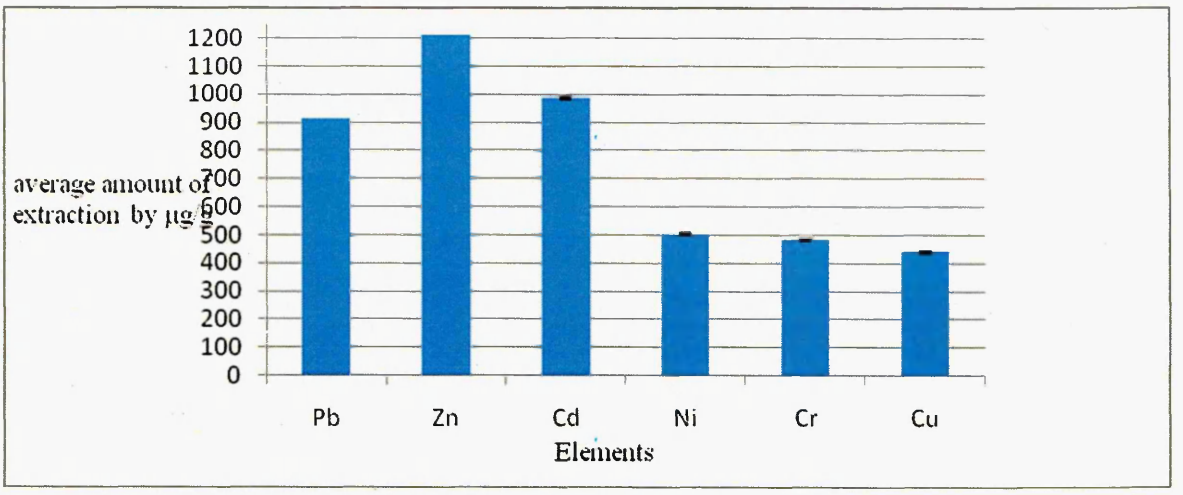

Figure 3. 4 Acid digestion test on 1g of soil contaminated by Pb, Zn Cd, Ni Cr, and Cu, 10min boiling , (5ml of acid+20ml water) as leaching fluid(n=3)

3.4.3 Effect of OPC on a solution contaminated with a mixture of metals

Examination of the effect of OPC on a mixture of metals in solution was carried out in the same manner as for lead in solution. Tables 3.9 and 3.10 show the effect of adding of OPC to mixture of metals solutions.The mixtures were prepared as in the same way as for the lead solution from nitrate salts $Pb(NO_3)_2$. All the metals were added to the solution as nitrate salts.

Table 3.9 Effect of OPC on mixtures of heavy metals in 50 ml of 100mg/l solution

Sample	pH	Pb (mg/l)	Ni (mg/l)	Cd (mg/l)	Cr (mg/l)	Al (mg/l)	Cu (mg/l)	Mg (mg/l)	Ca (mg/l)	Na (mg/l)	K (mg/l)
0.1g of OPC+ 100mg/l of mixture	8.69	0.10	0.21	0.091	0.37	1.43	0.29	1.23	634.5	3.21	9.8
0.1g of OPC+ 100mg/l of mixture	8.27	0.01	0.21	0.028	0.37	1.24	0.27	1.28	670.07	3.48	10.17
0.1g of OPC+ 100mg/l of mixture	8.62	0.102	0.208	N/D	0.36	2.3	0.27	1.16	675.8	3.6	10.29
Mean	8.52	0.101	0.211	0.06	0.36	1.33	0.28	1.22	660.1	3.4	10.08
Sd	0.22	0.001	0.003	0.19	0.00	0.59	0.009	0.060	22.37	0.19	0.25

N/D Not detectable,

The pH plays a major role in the stabilization of mixtures of metals. When any metallic element is immersed in a solution there is a pH value for the solution at which that element begins to be soluble, below that pH level the metal is insoluble. Table 3.10 shows the results when the pH level of the solution is between 5-6. At this value, nickel and cadmium are not soluble but the remainder of the elements shown are. Conner and Hoeffner [1998] have reported that the maximum pH for solubility of nickel and cadmium is 10.2 and 11.2, respectively. They concluded, more generally, that there will always be a compromise in

the selection of a pH value when dealing with mixtures of metals, because the solubility values for any two metals will not have minima at the same pH. The Zn was in negative value so it was not reported in this Table 3. 9.

It is clear that the removal of the metal ions gradually increases with increase in the pH level until an equilibrium range from 2.5 to 4.5 is reached. The percent removal slightly decreases with increasing pH value; this may be due to metal cation hydrolysis. The chemical analysis of OPC shows that sodium and potassium oxides have a dominant effect on the increase of the pH of the aqueous solution. El-Awady and Sami [1997] are in agreement with this suggestion.

Table 3.10 Effect of OPC on a mixture of: Fe, Al, Zn, Cu, Pb, Cd, Ni, and Cr, in solution containing 100mg/l of each element in 3 separate experiments

Sample	pH	Pb (mg/l)	Zn (mg/l)	Ni (mg/l)	Cd mg/l)	Cr (mg/l)	Al (mg/l)	Cu (mg/l)	Fe (mg/l)	Mg mg/l	Ca (mg/l)	Na (mg/l)	K (mg/l)
0.1g O.P.C+100 mg/l mixture	5.9	N/D	12.4	41.2	62.3	N/D	N/D	N/D	N/D	2.6	641.1	3.2	9.1
0.1g O.P.C+100mg/l mixture	6.0	N/D	5.2	35.0	59.8	N/D	N/D	N/D	N/D	2.9	671.9	2.8	9.1
0.1g O.P.C+100 mg/l mixture	5.7	N/D	15.3	46.1	66.2	N/D	N/D	N/D	N/D	2.7	627.6	2.8	8.2
Mean	5.9		11.0	40.7	62.8					2.7	646.8	2.9	8.8
Sd	0.1		5.2	5.6	3.2					0.2	22.7	0.2	0.5

Although the ion exchange occurred during mixing water with lead and also with adding the cement to lead solution, however according to .Jing. et al [2004] the following reactions occur in aqueous solutions:

$Pb^{2+} + H_2O = PbOH^+ + H^+$

$Pb^{2+} + 2H_2O = Pb(OH)2(aq) + 2H^+$

$Pb^{2+} + 3H_2O = Pb(OH)_3^- + 3H^+$

$Pb^{2+} + 4H_2O = Pb(OH)_4^{2-} + 4H^+$

$2Pb^{2+} + H_2O = Pb_2(OH)_3^+ + H^+$

$3Pb^{2+} + 4H_2O = Pb_3(OH)_4^{2+} + 4H^+$

$4Pb^{2+} + 4H_2O = Pb_4(OH)_4^{4+} + 4H^+$

$Pb^{2+} + 2CO_3^{2-} = Pb(CO_3)_2^{2-}$

$Pb^{2+} + CO_3^{2-} = PbCO_3(aq)$

$Pb^{2+} + CO_3- + H+ = PbHCO_3^+$

During the mixing of the lead with water some lead hydroxide will be formed, as in previous chemical equations. However,the precipitation reaction will result in solid state known as the crystallisation state. The reaction of lead with calcium carbonate which normally results in lead carbonate or lead bicarbonate according to Peter et al [1984] as described in the following equations :

Precipitation reactions

$Pb^{2+} + CO_3^{2-} = PbCO_3(s)$

$3Pb^{2+}\ CO_3^{2-} + 2H_2O \rightleftharpoons Pb_3(CO_3)_2(OH)_2(s) + CO_2^{+}$

$Pb^{2+} + 2H_2O = Pb(OH)_2(s) + 2H^{+}$

The expectation is formation of calcium carbonate since there is a large amount of Ca in the final solution. The amount of Ca was 646mg/l in the final solution after filtration by 542 Whatman. In Table 3.10 is shown the results of the effect of 0.1 g of OPC on a mixture of heavy metals. Some element was not detected in the final solution, e.g. Zn due to mixing with the OPC, which is a resulted in increasing in the pH, however each element has pH value where it will be dissolute and soluble. However in general terms, when the pH is above or near 6 most elements begin to dissolute and mobilise, according to Rutton et al.,[2008] the Zinc was removed from water at pH 10, the increase of the pH is associated with the amount of Ca in the solution. The reduction of Cd and Ni were 38% and 60 % respectively, at pH 5.9, at pH 8.5, the Cd and Ni were totally removed from metal solution in this current study(see Table 3. 9).

3.5 Characterisation of Precipitated Materials

3.5.1 Fourier Transformation Infrared Spectroscopy

The reference spectra, for potassium bromide KBr. This shows an obvious gradual decrease as the wave number increases, with a number of peaks and troughs superimposed, representing Potassium Bromide. For example there is a broad peak ranging from about 500 to about 1000cm^{-1}, with the remainder of the spectrum showing some smaller peaks and troughs. When KBr substrate is used as background (data no shown here).

When comparing the spectra obtained for contaminated soil and stabilised soil the FTIR spectra shows additional peaks. In each case the peaks due to the stabiliser material are different from the remainder. For instance, the spectra of OPC with lead contaminated soil

is different from the spectra of contaminated soil with lime. The difference in the curves can be ascribed to absorption that occurred in the surface of the contaminated soil with the stabiliser material.

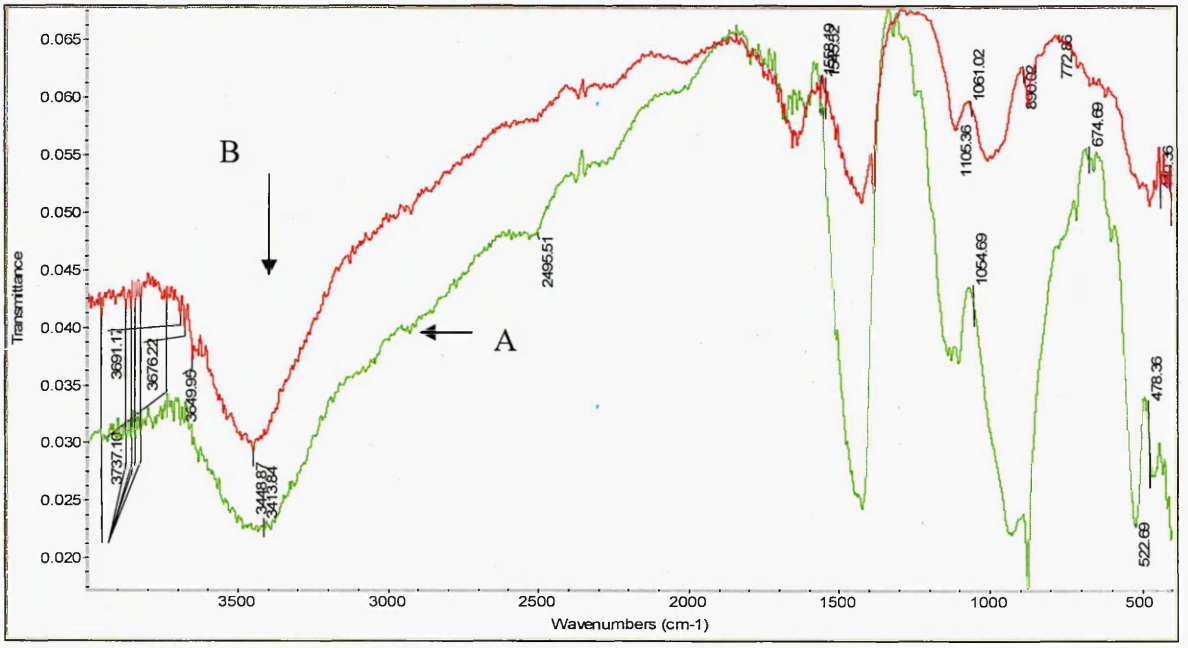

Figure 3. 5 FTIR plot of effect of OPC on lead solution, (A)- Spectrum for OPC, (B) -Spectrum for OPC stabilized lead solution

Figure 3.5 shows the spectrum for OPC only and OPC stabilized lead solution. The spectrum for dry OPC only, line A in green on the plot, is substantially different from the reference shown in KBr spectra due to the presence of the elements composing the cement, in particular Ca, Si, Al and Fe. There is a significant peak between about 500-800cm^{-1}, a sharp drop at about 900cm^{-1}, then a strong, broad peak from about 1000-3500cm^{-1}, which is interrupted by a marked trough around 1500cm^{-1}.The only peaks differ is 873 cm^{-1} which is not shown on the OPC peaks according to Table 3.11. Barnett et al [2002] the peaks are assigned to V2.CO3^{2-} that means $PbCO_3^{2-}$ has been formed as results of adding the OPC to lead solution at 1480 cm^{-1} and 870 cm^{-1}. Molah and Cock [1993] in agreement with finding . This curve everywhere falls below the FTIR spectrum for OPC stabilized lead solution, line B in green on the plot. A comparison of the two curves A and B show that lead formation in the samples, is responsible for the band 800-1100cm^{-1}, see Table 3. 11 and also Molah and Cocke [1993] reported v 4 (Si-O-Si) and v 2 (O-Si-O) between 795 and 465 cm $^{-1}$ and stated peak at 1080 cm $^{-1}$ is due to v 3 (Si-O-Si or Si-O-A1,

however it can be summaries The formation are deformation (V2)H–O–H,(V2).CO_3^{2-}, which it can be attributed to lead carbonated hydroxide, Pb.CO_3-OH.

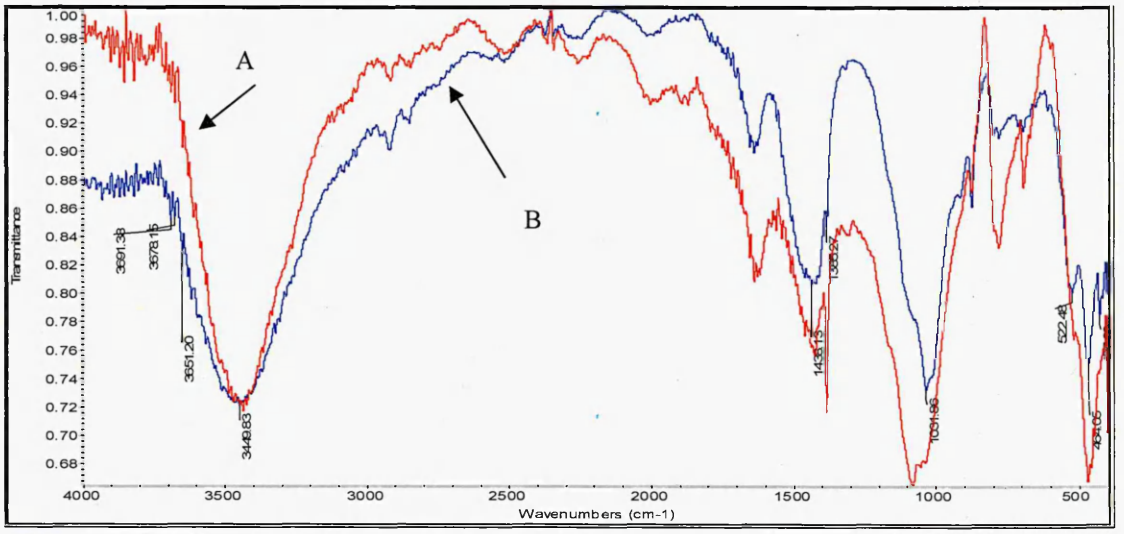

Figure 3.6 FTIR for soil contaminated with Pb and contaminated soil after treatment with OPC, (A) -Spectrum for lead contaminated soil, and (B)- Spectrum for contaminated soil treated with OPC

Figure 3.6 shows the FTIR spectra for soil contaminated with lead and the contaminated soil treated with OPC. Naturally, the curves show marked similarities. There is a broad band from about 3200cm^{-1} to about 1000cm^{-1}, which is composed of a number of overlapping causes which are listed in Table 3.11. There is a second sharper and somewhat spikey peak from about 1000cm^{-1} to about 400cm^{-1}. The distinct spike at about 800cm^{-1} can be assigned to carbonate (CO_3) according to Barnett et al [2002] and Hughes and Metven [1995], who investigated the composition of cement. The peak at 1438cm^{-1} in Figure 3.6 can be attributed to only $PbCO_3$ [Yılmaz and Olgun 2008]. In support of this finding, also the small peaks at 460-1200cm^{-1} are evidence of the presence of SiO_4^{2-} and V-Si-O which is in agreement with XRD investigation (see section 3.5.4).

Qian et al [2008] have shown Ca and OH precipitation around 900cm^{-1}, a stretching vibration ascribed to OH may also account for the absorption bands around 3638cm^{-1}. The band around 1640 cm^{-1} was an H–OH vibration ($\nu 2H_2O$) of interlayer water for the Friedel phase, whereas the broad band at 3442cm^{-1} was due to a vibration (νOH) in structural water. For the pure Friedel phase, a very strong feature at around 786 cm^{-1} is an Al-OH bending mode [Qian, et al 2008] and [Birnin-Yauri and Glasser, 1998]. The band at 876cm^{-1} represented the presence of symmetric and asymmetric vibrations of the Al–OH band in the $Al(OH)_6$ octahedral structure of ettringite in fly ash–CSA cement matrices. But

the frequency of the Al-OH band for pure ettringite was at 872 cm^{-1}. This difference might be another proof of heavy metals such as Pb fixed in the structure of ettringite. Chloride does not absorb in the range 400–4000 cm^{-1}. [Qian et al 2008]. According to [Yılmaz and Olgun 2008] the band 1106–1116 cm^{-1} is assigned to the stretching vibration (v_3) of gypsum SO_4^{2-}. In this study Peaks at 1101 cm^{-1} in Fig.3.5 can be assigned to sulphate.

Table 3.11 Principal FTIR frequency bands in hydrated Portland cement [Barnett et al [2002] compared with results of this study

Wave number (cm^{-1})	Assignment	Soil+ Pb +OPC in this study	OPC+Pb solution in this study
3645	stretching O-H of Ca(OH)2	3600-3701	
Zone 3100-3400	symmetric and asymmetric stretching (Vl and V3 of O-H	3020-3417	3431
1650	Deformation(V2)H_O_H	1567-1590	
1480	V3.CO_3^{2-}	1440-1670	1421
872	V2.CO_3^{2-}	792-1024	874
712	V4.CO_3^{2-}	769-757	772
970	stretching Si-O(V3),(in polymeric unit of $SiO4^{4-}$)		
925	stretching Si-O(V3) (in non-hydrated cement)		925
522	V4.Si-O	461-503	520
452	V2.Si-O	468-601	456
1115	V3.SO_4^{2-}	1093-1105 1174	1110

3.5.2 Raman Spectroscopic Analysis

The results of the measurements carried out on the OPC sample are shown in Figures 3.7 and 3.8. Raman spectroscopy is sensitive to the presence of the calcium carbonate; it thus offers a ready assessment of the extent of its presence in the samples and is a useful technique for finger-printing of the material Potgieter-Vermaak et al [2006]. This is seen by comparing the two curves in Figure 3.7 the one for 0.1g OPC in a solution of 50ml of DI water, the other with lead added to the OPC in solution.

Figure 3.7 shows only one strong peak at 1040cm^{-1} which can be attributed to the lead-silicate-carbonate group, the gypsum present in the sample. The gypsum was identified as calcium sulphate dehydrate by the symmetric vibration of the sulphate ion observed at 1007cm^{-1}, as well as the anhydrite at 1023 cm^{-1}. KirkPatrick et al [1997], according to Table 3.12, the group present is lead silicate carbonate.

Figure 3.8 shows the Raman spectra of soil contaminated with lead, and soil contaminated with lead that had been subsequently treated with 0.1g OPC powder. The figure shows very similar peaks, except at 1000-1050cm^{-1} where the contaminated soil sample shows a strong peak, which is due to the lead silicate carbonate group according to [KirkPatrick et al 1997] and Gibbs et al [2010] is $2PbCO_3.Pb(OH)_2$. The lead had reacted with the silicon and carbonate present in the soil. The v_1 and v_4 vibrations of the carbonate were observed at 1084cm^{-1} and 712cm^{-1} respectively, and the lattice vibration at 280 cm^{-1} is due to Ca-O, Portlandite.

Kirkpatrick et al [1997] are in general agreement with these results. There was the agreement on peaks of 462 cm^{-1} where he reported that internal deformations of Si-O,tetrahedra(O-Si-O bending) between 430-540 cm^{-1}. Also from comparison of the two spectra it is obvious that there are not nearly as many peaks as obtained by FTIR or XRD. This is be attributed to the lower laser efficiency.

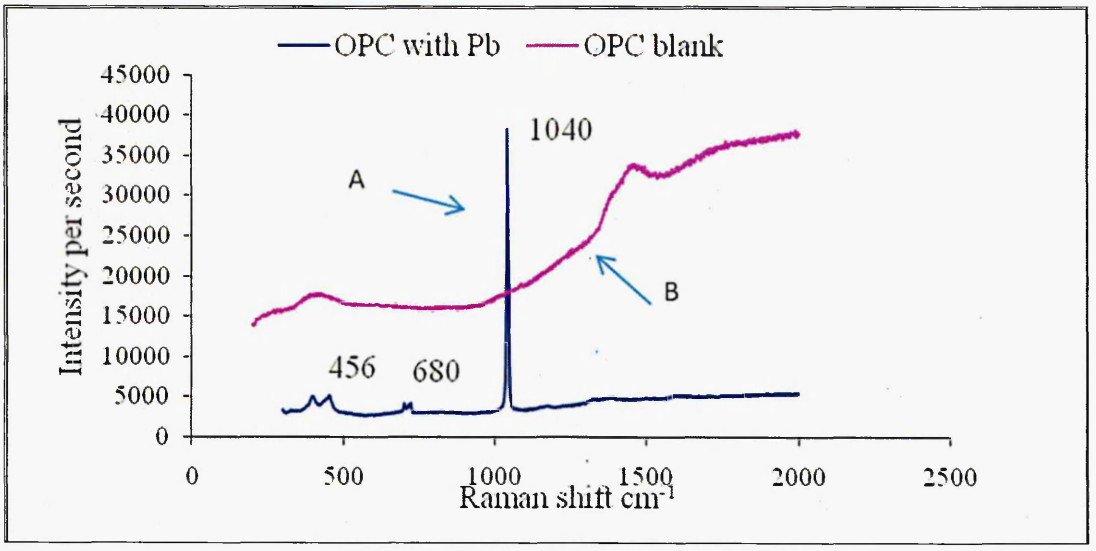

Figure 3.7 Raman spectra for: (A) - 0.1g of OPC in 50ml of lead solution, strength of lead solution 20g/l, (B) – 0.1g of OPC in 50ml DI water.

The spectra of the calcium aluminate phases on the other hand, were comparable and seemed to be independent of laser excitation wavelength. The major Raman peaks were identified at 456 cm^{-1} and 680cm^{-1} and 1040 cm^{-1}. According to Bersania et al [2008] plumbonacrite - $Pb10(CO_3)6O(OH)$ - gives peaks at 1047cm^{-1} and 460cm-1, and the peaks at 450cm^{-1} and 680cm^{-1} are due to $PbSO_4$ and lead carbonate.

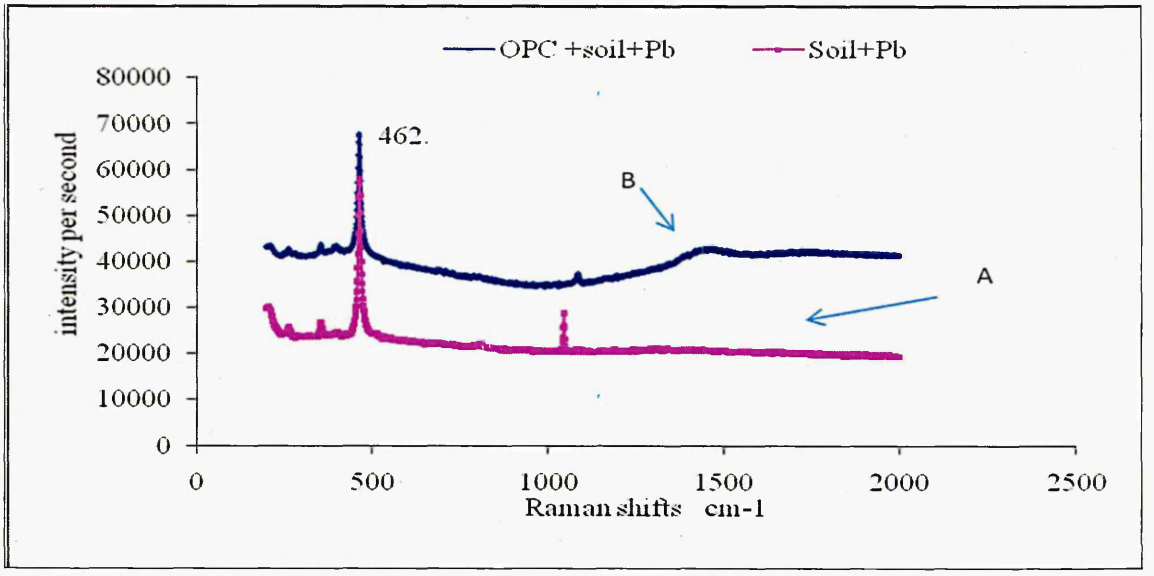

Figure 3.8 Raman spectra for: (A) - soil of mass 5g contaminated with 20,000mg/l of lead , (B)– as A but treated with 0.1 g of OPC

Table 3.12 Raman frequencies of the principal bands in hydrated Portland cement (after KirkPatrick et al 1997)

Band	Origin	Lead contaminated soil treated with OPC in this study	OPC stabilized Pb solution in this study
200-400cm^{-1}	Ca-O vibration		320-360cm^{-1} = Ca-O = Portlandite
430-540cm^{-1}	Internal deformations of si-O,tetrahedra(O-si-Obending)	462 cm^{-1}	430-540 cm^{-1}
600-700cm^{-1}	silicate group		
800-1100cm^{-1}	symmetrical stretching of silicate tetrahedral carbonate group) Symmetrical stretching (SS) of Si-O tetrahedral.	1044 cm^{-1}	976cm^{-1} (Si-OH) Pb, Si, Ca
3000-4000cm^{-1}	OH vibration		

3.5.3 XRD investigation

As there was experimental evidence of precipitation of metals on the surface of the beaker and the filter (see Section 3.4), it was useful to characterise the chemical structure of these metals. It has been reported that in many cases hydroxide compounds form on the surface of the mix of lead contaminated soil and OPC. The XRD examined the soil contaminated with lead and treated with OPC, in comparison with the soil sample containing OPC but no

contaminant lead. The results of the analysis suggest that $PbCO_3$ or $Pb(OH)_2$ may have formed on the surface. This is not unlikely as the main constituent of OPC, over 60%, is $CaCO_3$.

Samples were ground to a fine powder using a mortar and pestle, and were mounted on plastic sample holders. All samples were studied for reflections (2theta) in the range 10^o to 80^o and scan rate were for 2 hours. Figure 3.10 shows the XRD spectra obtained for uncontaminated soil with added OPC, and soil contaminated with lead with added OPC. In Fig.3. 9, the compounds present were identified by comparison with an international XRD database [http://www.cds.dl.ac.uk]. The strongest peaks for the lead contaminated solution and lead with added OPC was at 17.868^o and referred to lead sulphate, $Pb_2(SO_4)$. The other strong peaks are due to the presence of $Pb(SiO_3)$. Other compounds were $PbCO_3$, and Plumbonacrite, $Pb_5\ O(CO_3)_3\ (OH)_2$-[P63CM]. The peak at 22.86 can be referred to an unnamed compound $Pb(H_2O))(C_2O_4)(H_2O)$. The peak at 71.776^0 is taken to show the formation of Hydrocerussite. Figure 3.10 also shows the formation of lead hydroxide monohydrate, according to the Cambridge XRD data base. Asavapisit et al [1997] have reported formation of OPC + $Pb(OH)_2$ at 17.8^o peaks.

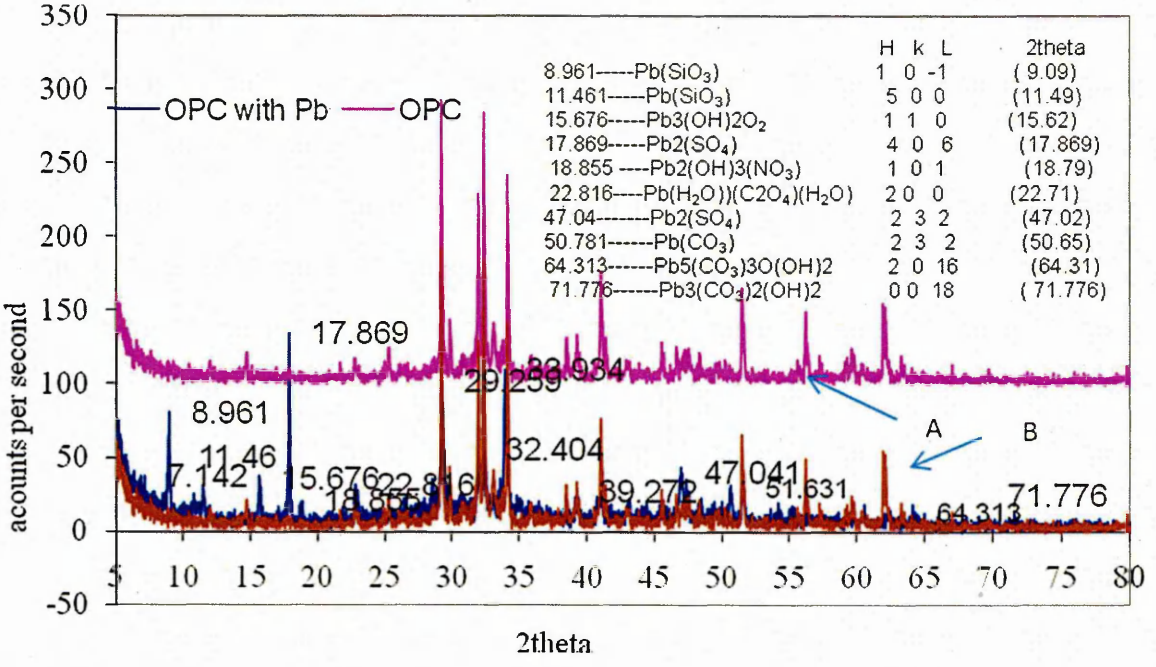

Figure3.9 XRD investigation of the effect of OPC on lead solution, (A) Spectrum for OPC, (B Spectrum for OPC stabilized lead solution

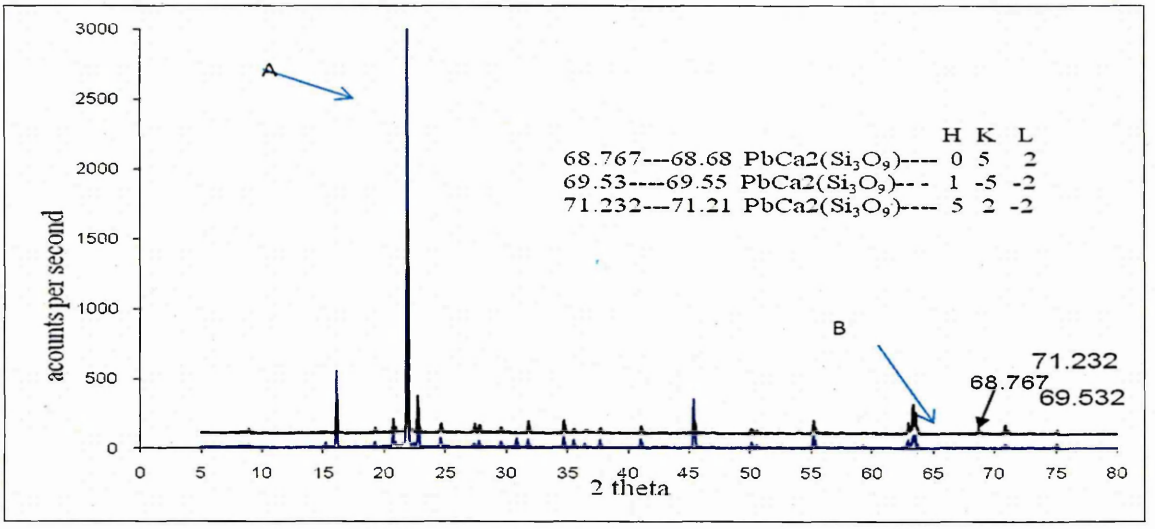

Figure 3.10 XRD investigation for soil contaminated with Pb and contaminated soil after treatment with OPC, (A) spectrum for lead contaminated soil, and (B) spectrum for soil treated with OPC

An explanation of this formation is that most of the lead had been digested and bound by Ca, Si and Al, in the form of carbonates, silicates, sulphates, sulphides and hydroxide. The Environmental Scanning Electron Microscope (ESEM) map micrographs in section 3.4.5 in this study support this idea, the compounds being formed during the curing of the sample for 7 days. These results agree with Dongjin [2007] who reported that lead carbonate, lead carbonate hydroxide hydrate and sulphate hydroxide ($Pb_4SO_4(CO_3)2(OH)_2$) in cured experimental samples.

Minocha et al [2003] investigated the important constituents of cement (including products of hydration) and identified, amongst others, tri-calcium silicate (C_3S), di-calcium silicate (C_2S), and calcium hydroxide ($Ca(OH)_2$). However, according to the crystal model provided by Minocha et al [2003], when C_3S is in contact with water, the calcium silicate mineral dissociates into charged silicate and calcium ions as in the following equation, see Chen et al [2009]:

$$C2S + 3H_2O \longrightarrow Ca^{2+} + OH + H_4SiO_4$$

$$\longrightarrow C\text{-}S\text{-}H + Ca(OH)_2$$

The results of this study are supported by the findings of Cao et al [2005] whose tests showed the formation of cerussite ($PbCO_3$) and/or hydrocerussite ($Pb_3(CO_3)_2(OH)$). The

XRD shown in Figure 3.10 for soil with OPC added indicates urban soil to contain mostly calcite ($CaCO_3$) and quartz/sand (SiO_2), with small amounts of kaolinite ($Al_2Si_2O_5(OH)_4$. There is no sign of lead formation in the samples and this can be attributed to a curing factor and physical binding between the OPC and the contaminated soil. This is in contrast to the curve which shows the soil containing both lead and OPC, and cured for 7 days in room temperature. The curing time is essential for the chemical reaction take place between the contaminant and stabilized material.

3.5.4 Environmental scanning electron microscope (ESEM)

3.5.4.1 SEM results

Many researchers (see Diamond 2004), have concluded that no other technique can provide the same depth and breadth of information, in particular with use of backscatter-mode SEM.

In this study given the structure of Pb contaminated cement, and OPC with no added lead solution, in Figure 3.11a the lead has had no apparent effect on the cement morphology, though the cement may only coat the surface. This is supported by mapping micrographs for Ca and Si on the same samples which shows the association of lead with those elements, as in Figure 3.11b. The EDX, Figure 3.11b, shows the presence of lead amongst other elements in the cements, suggesting that lead bound inter-particles of cement may be attributed to the distribution of lead through the C-H-Si matrix.

In Figures 3.12 and 3.11, which show the ESEM Micrographs for OPC powder and OPC stabilized lead solution, no indication of the presence of lead could be detected on the surface of the OPC powder. Figure 3.11 shows metal on the surface and the OPC shows an inter-granular fracture. Figure3.11b also shows the EDX spectrum OPC stabilised lead solution which confirms the presence of lead in the specimen. It was conducted using the reference samples of OPC and comparing these with OPC stabilized Pb. The results of Halim et al [2004] support this analysis in images of the OPC stabilized Pb. Dongjin [2007] also supported this result when he observed the very low proportional of lead in the surface within the elements of the cement, Ca, Si and Al by quantitative measurements using X-ray.

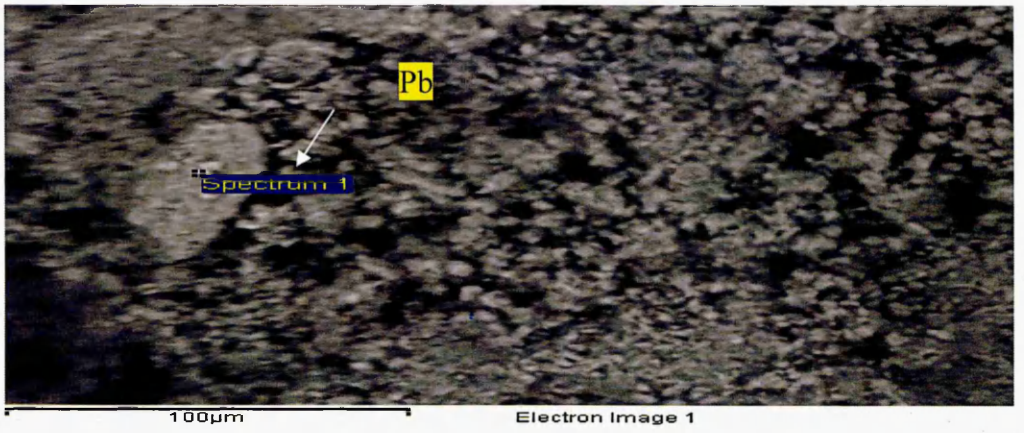

Figure 3.11 a ESEM image for OPC stabilized lead solution, Pb at spectrum1

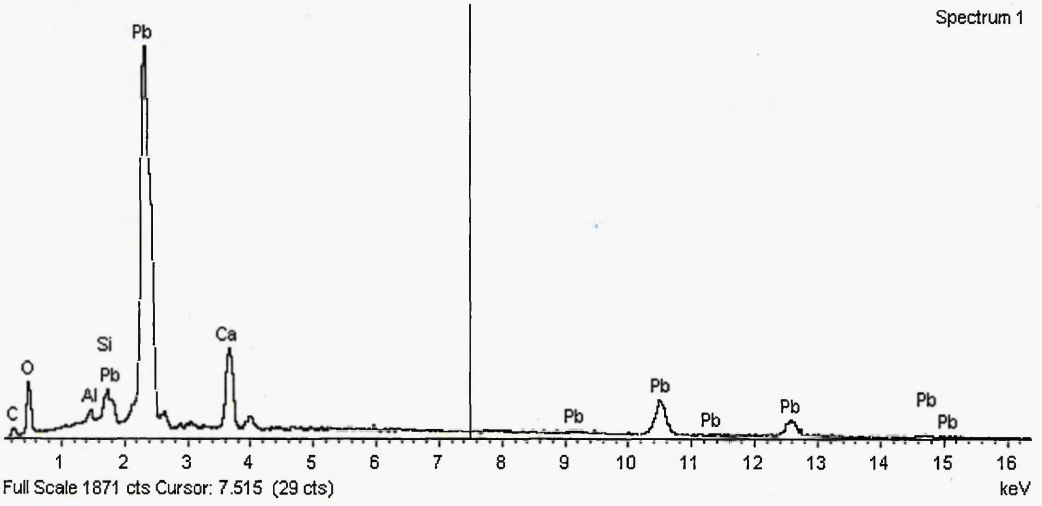

Figure 3.11 b EDX map of ESEM image of OPC stabilized lead solution, spectrum 1 Pb .associated element (Pb, Al, Si, Ca, O, and C)

Secondary phase analysis of the specimen was required, with backscatter, to give more resolution and the acceleration energy used was 15 kV. Figure3.11 present the difference in the treated sample against the reference sample according to Chen [2009] who has reviewed the classification of Thevanin and Pera [1999]. The presence of lead in the EDX is quite clear in support of this argument. Condeles et al [2006] have shown the presence of metals using EDX and backscatter to investigate crystal growth. That the basic structure of cement is dominated by the presence of C-S-H is shown in the image by the light grey regions. These particles contain Ca and Si. Bonen and Sarkar [1995] and Bone et al [2004] have indicated that heavy metals may physically be encapsulated in the C-S-H matrix.

Figure 3.11 is the result of using the ESEM to view the lead present in OPC. Also EDX shows the presence of a high lead content in the specimen that formed on the surface of the filter, which itself shows the presence of lead in the sample, confirming the results of the other techniques (ICP, FTIR, Raman and XPS) identifying the formation of lead compounds. There is no indication of the presence of lead in cured samples, see Figure 3.14a, because of the association of lead into the cement where it formed $PbCO_3$, $PbSO_3$, and $PbSO_4$. The Raman spectroscopy and FTIR results confirm this (Fig.3.5, 3.6 , 3.7).

Figure 3.12a shows the image obtained from the ESEM and the spectrum obtained with the lead contaminated soil treated with OPC and show the effect of OPC when stabilizing contaminated soils. Figure 3.13a shows the image of the SEM and spectrum for lead contaminated soil. The ICP, FTIR, Raman, XRD and XPS results support these results. Figure 3.13 it shows the same sample but at different spectrum that presents more lead peaks. See EDX (3.12b), which demonstrates the important of magnification and selected working distance of selection and spot size to identify the elements in the specimen.
Figure 3.14a shows the ESEM image for the investigation of solidified OPC contaminated with Pb solution and cured for 7 days, at different working distances to monitor the scan of the specimen image and from 60 μm to 100 μm distances from the specimen. There is no evidence of the presence of Pb in the samples. Figure 3.14 b, which is the corresponding EDX spectrum shows no Pb present. This demonstrates that after being cured for 7 days in the plastic mould almost all of the Pb had been bound in the cement matrix by Ca, Al, Si, etc. In addition, the ICP results for the leaching test also show that only a small amount of Pb leached out compared with initial dosing of 20g/l of Pb solution. It can be seen from the ESEM and EDX results that the cured samples are lead free, see Fig.3.14 for non-cured samples. The OPC stabilized and mobilized the lead but it was not digested within the OPC matrix, which the curing allowed the material and the contaminant to react. The curing time and solidified nature of the OPC stabilized and solidified the lead, holding the lead in the mould for a sufficient period of time for the lead to react within OPC matrix to form compounds such as Pb CO_3 or Pb SO_4, etc. In the ESEM investigation the results reported for ESEM analysis for OPC which was not cured showed free lead on the image, see Figure 3.11 This was mobilisation of Pb to the surface not encapsulation within the cement matrix. Solidification would occur only during contact between the OPC and the lead solution in the mould, under the same conditions of temperature, humidity, etc. However the acid digestion test shows the present of lead in the sample see Table 3.16, In addition,

more investigation was carried out on the same specimens investigated by taking an extra image of ESEM and EDX spectra on second location of samples.

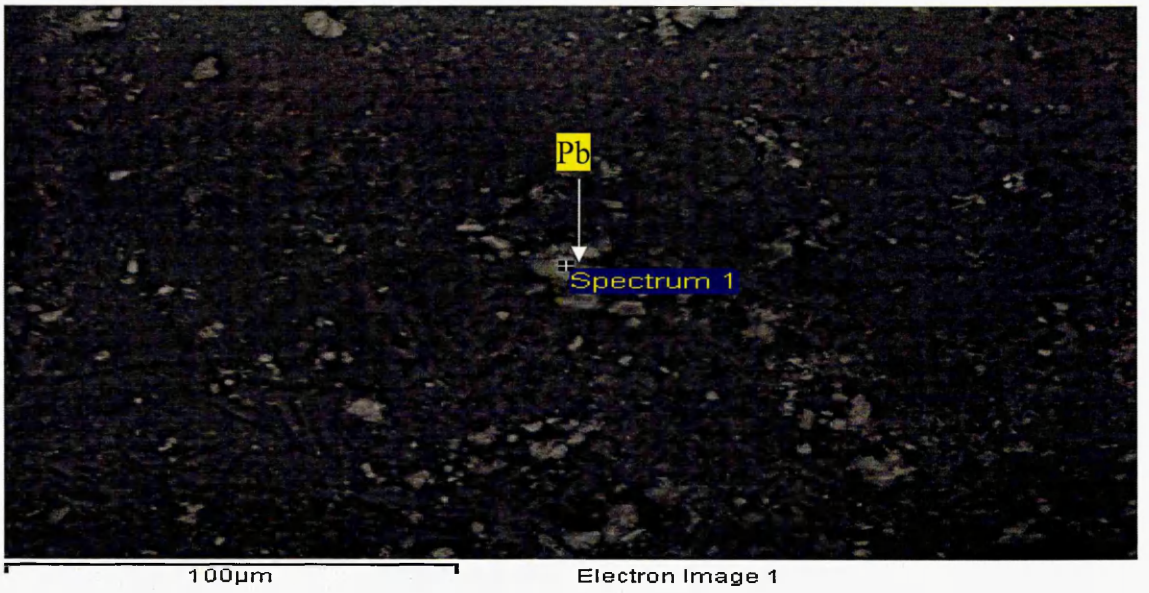

Figure 3.12 a ESEM images for OPC treated Pb contaminated soil, Pb at spectrum 1

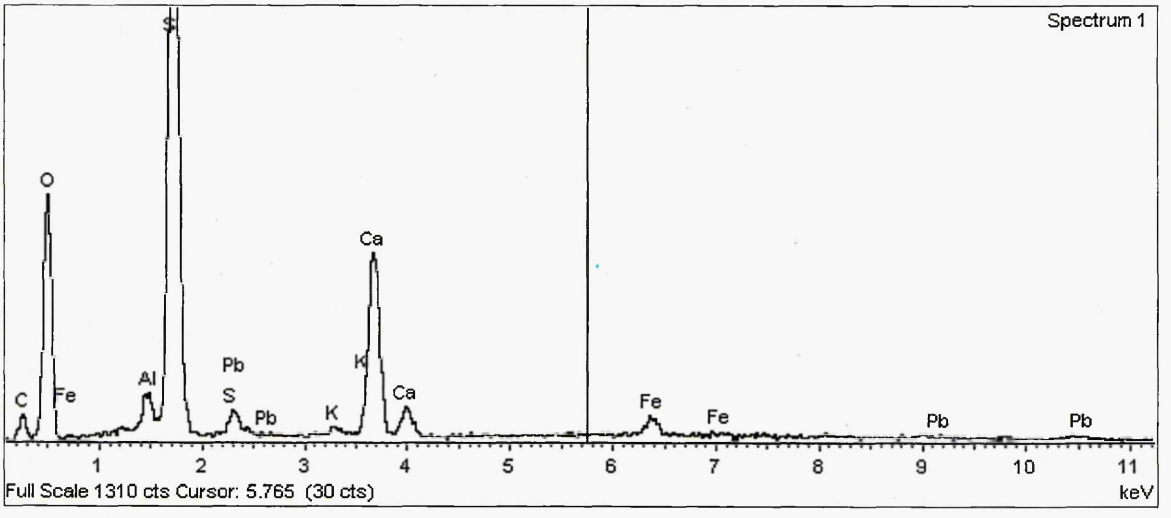

Figure 3.12b EDX spectra for ESEM image specrum1 for OPC treated Pb soil contaminated (Pb, Al, Ca, K ,S, Fe, O and C)

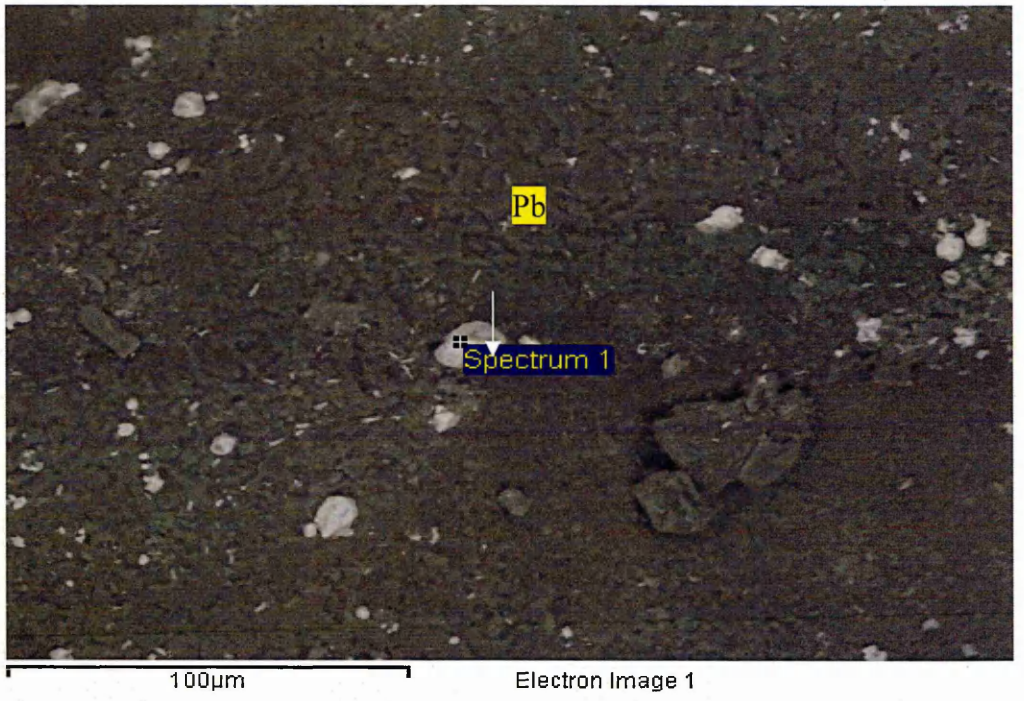

Fig 3.13 a ESEM image Pb contaminated soil, Pb at spectrum 1

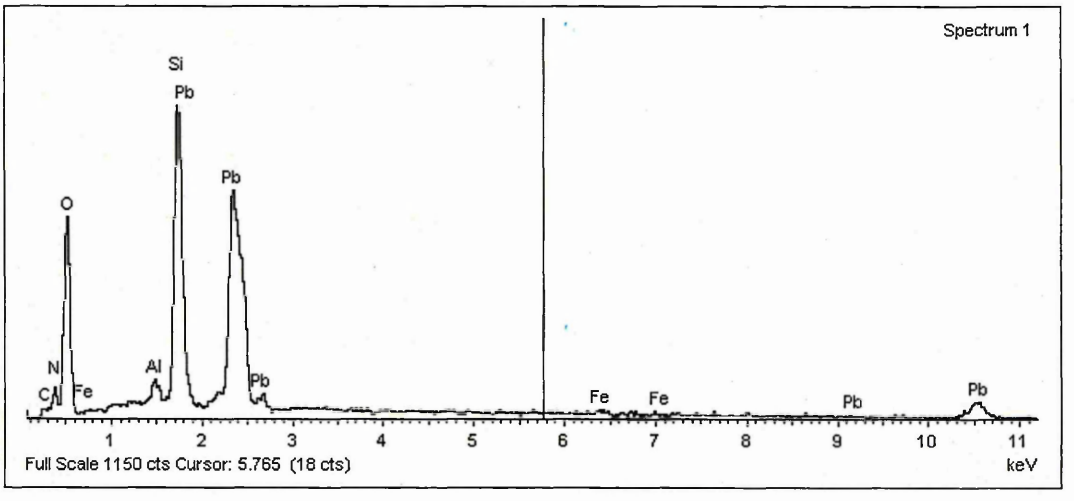

Fig 3.13 b EDX map for ESEM image at spectrum 1 for Pb contaminated soil element present (Pb, Al, Si, Fe, O, C, and C)

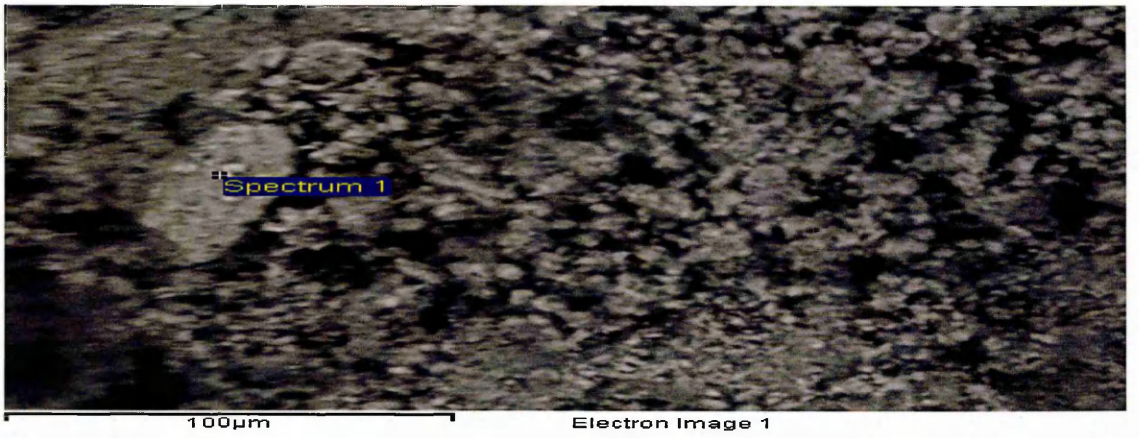

Figure 3.14 a ESEM image 1 for solidified lead by OPC cube, sample cured for 7 days. at 100µm working distance

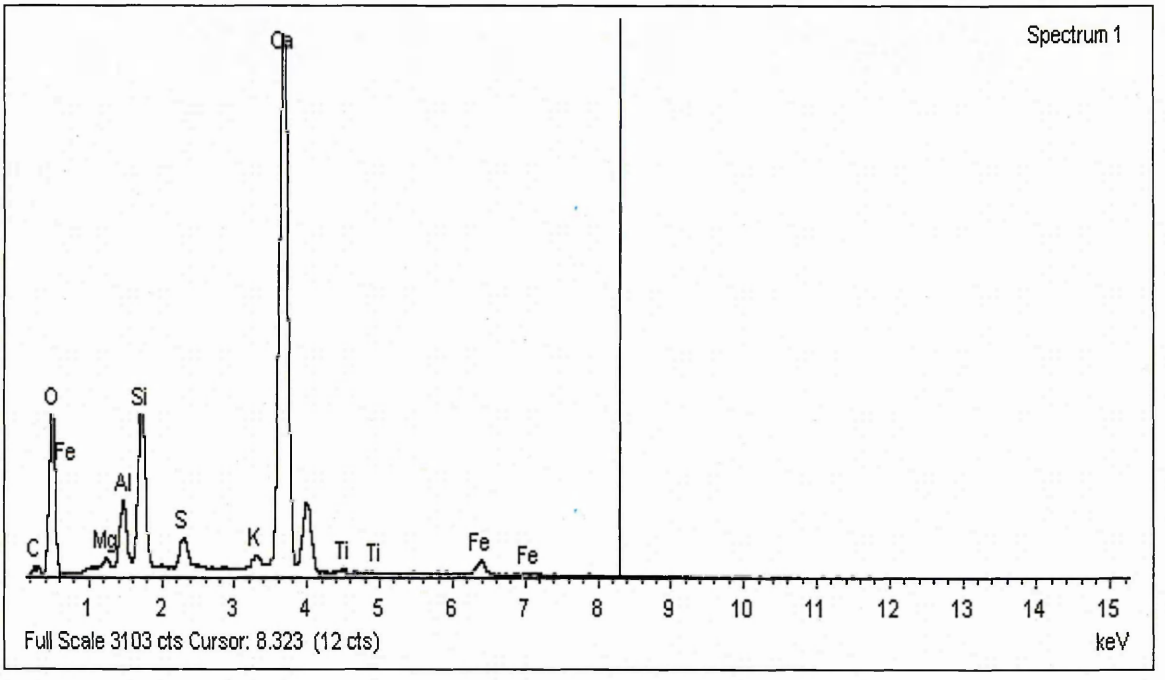

Figure3.14b EDX spectrum 1 for ESEM image of 0.1g of solidified OPC, contaminated with lead solution of strength 20g/l, sample cured for7 days (elements No, Pb ,Al,Si,K.Ca, Mg, Fe ,Ti.Ca and O).

3.5.5 X-ray photoelectron spectroscopy

3.5.5.1 Introduction

X-ray photoelectron spectroscopy XPS is widely used to investigate binding mechanisms of metal ions in cementitious materials Scheidegger et al, [2006] because it allows relatively straight-forward analysis of the near-surface of materials. It can offer significant micro-chemical information on material surfaces and is widely used Hulya et al, [2007]. Recent advances in XPS instrumentation have now made it possible to analyse small samples with improved spatial resolution and to make use of the so-called "imaging" XPS, where energies can be imaged with a spatial resolution of down to 3μm [James et al 2008]. The results of XPS imaging of the energy of the lead so-called 4f peak are shown in Figure 3.15 and 3.16. This peak is in fact of very small amplitude, and with the unaided eye is hardly discernible over the background.

3.5.5.2 XPS Contaminated Solution and OPC treated solution.

Figures 3.15 to 3.18 were obtained by using XPS on OPC and 0.1 g OPC stabilized Pb solution. Figure 3.17 shows a wide XPS scan on which can be seen a small peak which was identified as lead 4f. The lead 4f peak is, in fact, naturally shaped as a "doublet" (i.e., has two main peaks separated by 4.7eV) positioned at 138eV with an area 0.844 % occupied of the samples, and is the smallest of the peaks listed. Each of the two peaks of the doublet was further made up of separate peaks arising from the various chemical states of lead that were present.

In Figure 3.16 which shows the binding energy for uncontaminated OPC, no distinct peaks were found in the region of 138eV, the lead 4f peak, as there was no Pb present in the specimen.

On Figure 3.15 the peak Ca2p is seen at 346eV and had a 15.8 % of area. On Figure 3.17 the Ca2p was at 346eV but with a smaller area, 12.1%. This decrease in area was due to the presence of Pb in the specimen that ion exchange reaction may occurred between the Ca and Pb ions.

This is confirmed by Figure 3.18, which shows the binding energy over the range 130-148eV. The peaks at 137eV and 139eV were attributed to the lead 4f peak. According to international XPS data base the two peaks are due to the presence of $PbCO_3$ and PbOH. Tingle et al [1993] reported presented of Pb CO_3 at 138.3 eV. Mollah and Cock [1992] and

James et al [2008] support this suggestion, which is consistent with the results obtained from the other investigative techniques used in this study, e.g. XRD and FTIR, the leaching tests, and ESEM. All of which shows the presence of lead in samples.

Rha et al [2000] has reported that lead ions concentrate on the surface of slag and precipitate into salts such as carbonates, hydroxides, and sulphates. Because Pb salts have extremely low solubility, it was likely to work as a barrier between slag particle and water. For this reason the presence of lead ions retard the initial hydration of slag.

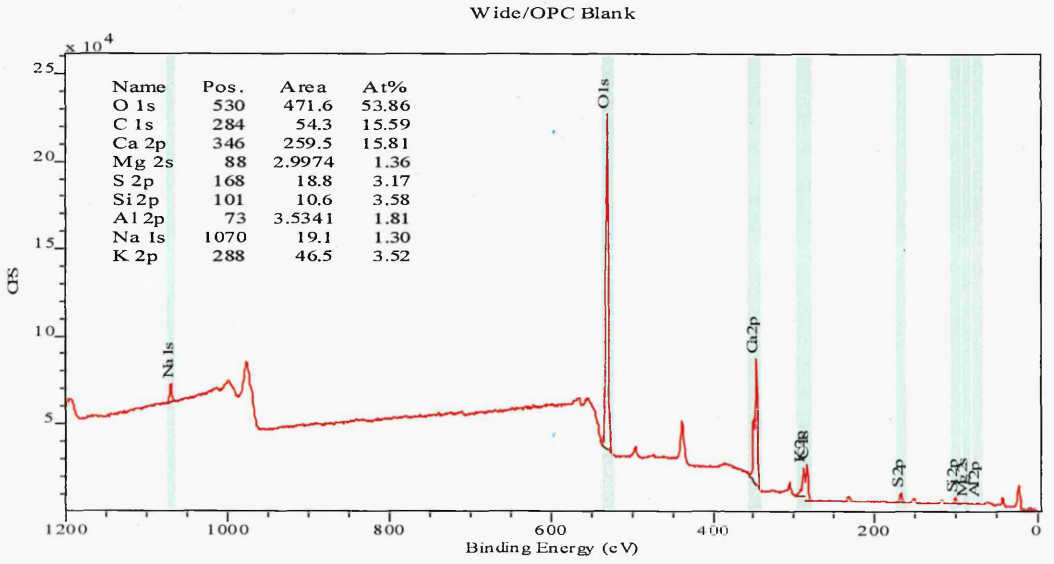

Figure 3.15 Wide scan of XPS spectra for OPC powder blank sample, no lead

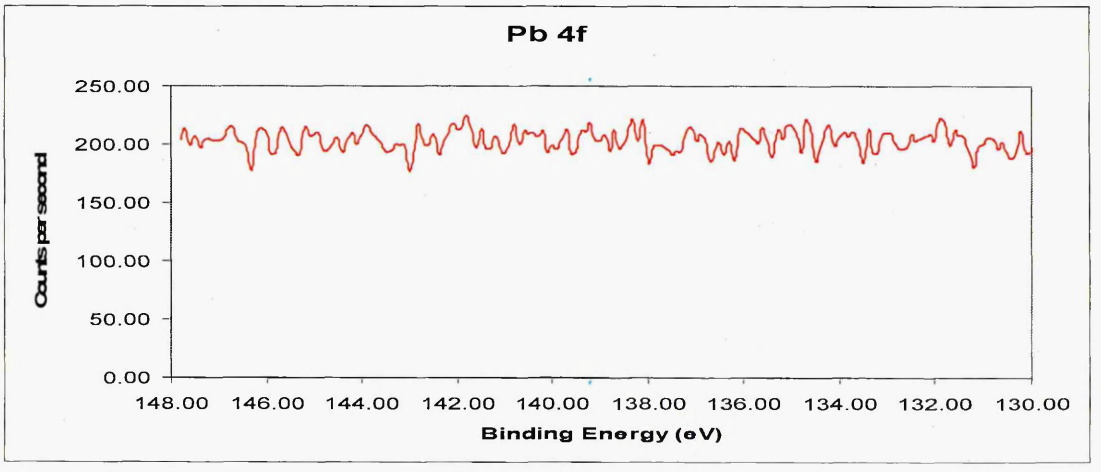

Figure 3.16 Detailed XPS analysis of the spectrum for OPC powder over the region of the lead 4f spectral line, on lead in blank sample

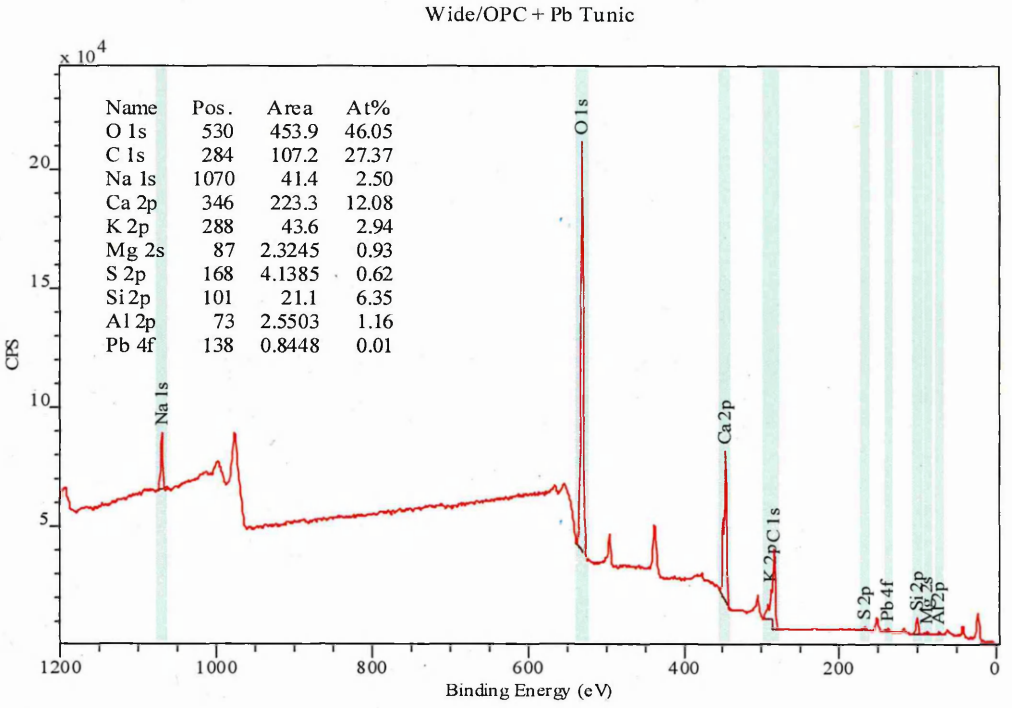

Figure 3.17 Wide scan of XPS spectra for cement matrix containing a stabilized Pb solution.

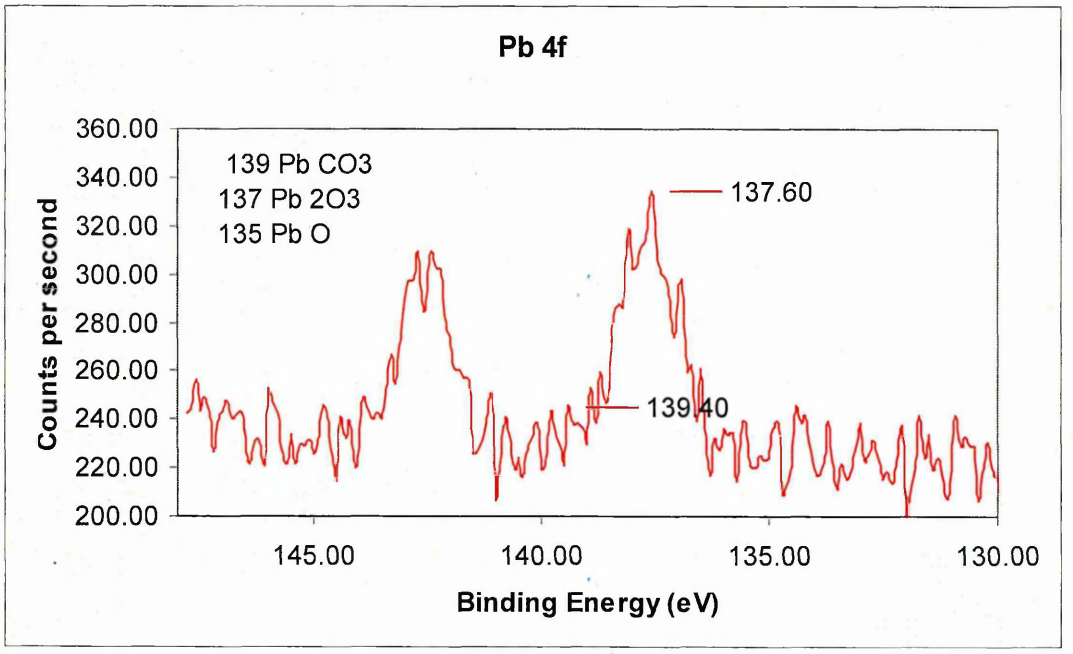

Figure 3.18 Detailed XPS analysis of the spectrum for OPC stabilized lead contaminated solution, over the region of the lead 4f spectral line

3.5.5.3 XPS contaminated soils and cement treated soil results

The Fig. 3.19 presents wide scan of lead contaminated soil, untreated, it shows clearly position of lead Pb4f at 136 eV occupied about 0.91 at %. The most of the elements were O 1 s, Si2p, and Na1s, which account, 55, 20, 4 % respectively while Ca2p only account 1.18. See Figure 3.19 and 3.20. However the peaks 136 eV are assigned to Pb4f7 according to XPS international data base. And 141 eV assigned to Pb4f5. In classification to the chemical state for those peaks and relaying on James et .al, [2008] the 137 eV and the doublet 141 eV are assigned to Pb O. Or Pb SO_3. Similarly the Fig. 3.21 show the wide scan of treated contaminated soil with 0.1g cement, comparing with none treated sample see Fig. 3.19 The Ca2p occupied 10% , the Pb occupied 0.74 % reduced from 0.91% in none treated soil. And Si to 13% from 20 % in none treated samples, the Pb 4f at peaks 136 doublet 141.2, in regard to James, et al. [2008] are assigned to $PbSO_3$, $PbSO_4$ which are similar in agreement with results obtained by XRD and FTIR. See section 3.5.2 and 3.5.4 and ESEM, 3.5.5. The shifting in binding energy in Fig 3.23.Distribution of lead Peaks over region of Pb4f spectra's is referred to different types of lead in Pb4f region that $Pb4f_{7/21}$ and $Pb4f_{5/21}$ and which are multi-compounds of lead , such as Pb, PbO, $PbSO_x$.

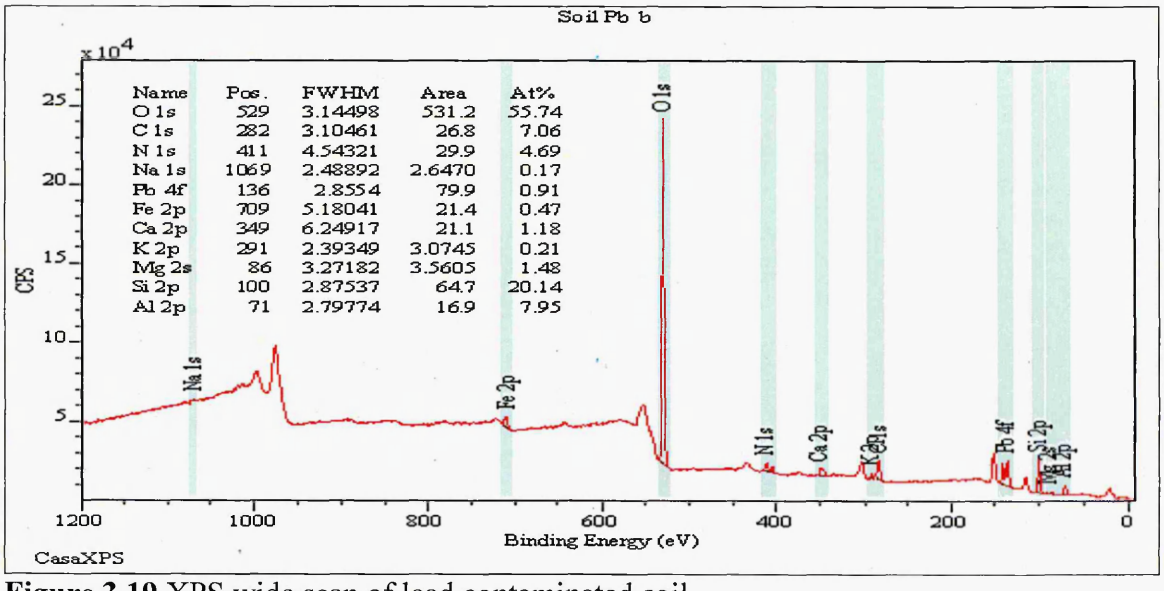

Figure 3.19 XPS wide scan of lead contaminated soil

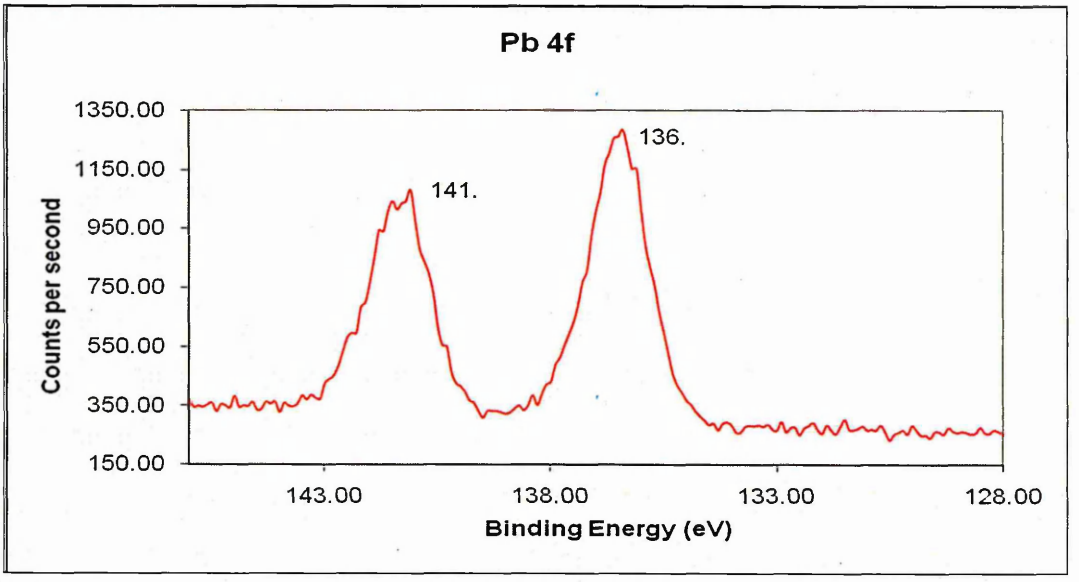

Figure 3.20 Detailed XPS analysis of the spectrum for lead contaminated soil, over the region of the lead 4f spectral line

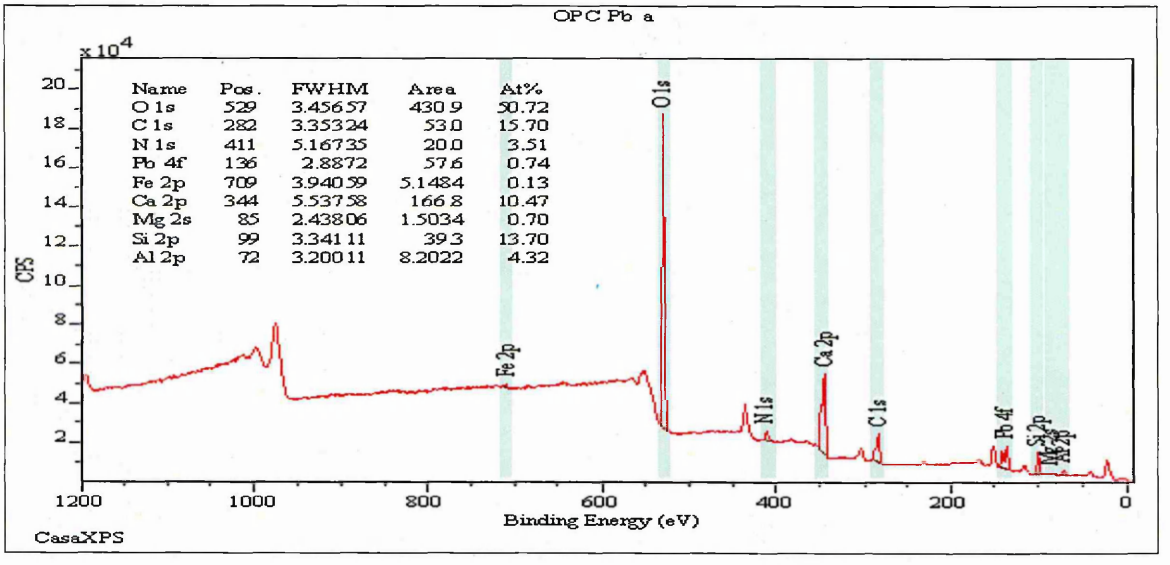

Figure 3.21 XPS wide scan spectra of 0.1 g of cement a stabilized 5 g of Pb contaminated soil.

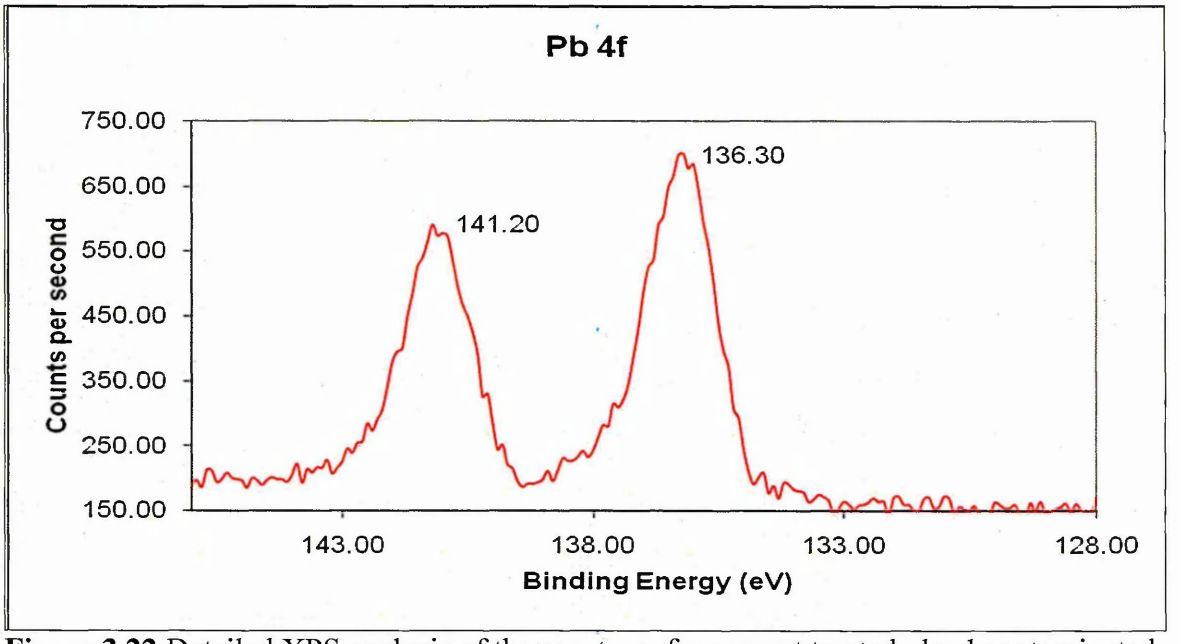

Figure 3.22 Detailed XPS analysis of the spectrum for cement treated lead contaminated soil, over the region of the lead 4f spectral line

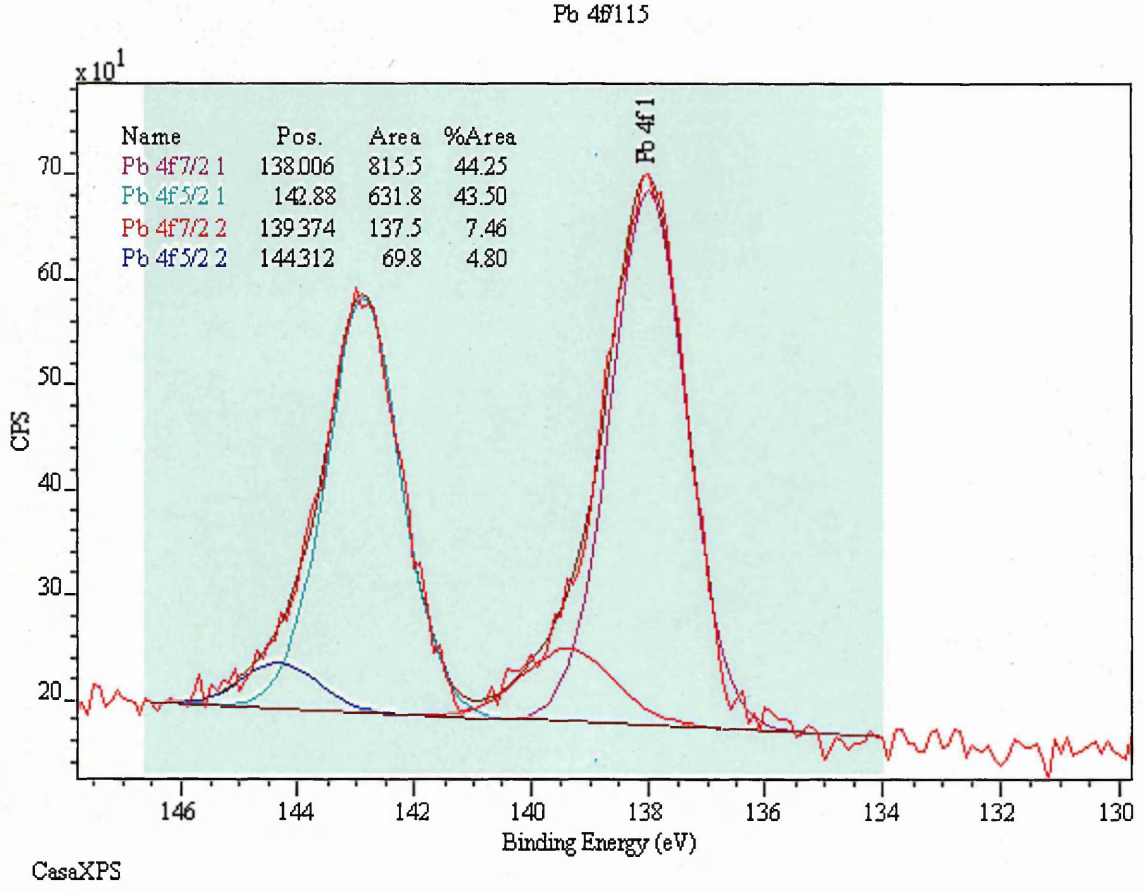

Figure 3.23 Distribution of lead Peaks over region of Pb4f spectra

3.6 Tank leaching test

3 .6.1 Background

The tank leaching was required in order to develop and understand the initial data obtained from the batch test, such as the role of the OPC and curing time in the chemical reaction. Most of the chemical reactions were set into the mould.

The tank test is essential to describe the soil remediation process because it is more closely representative of field conditions. Researchers in previous work have used the Semi-dynamic leaching test (tank test, the American Nuclear Society test ANS16.1). It has already been reported that the leaching of contaminants from a cement-based waste form is mostly a diffusion-controlled process which is known as a semi-dynamic leaching test aimed at predominately evaluating the release of metals in diffusion-controlled environments. By applying this test we get the cumulative fraction of leached materials versus time.

The tank test was found to be suitable for predicting the rate of the leaching from solidified samples of OPC under the same conditions for long term leaching. Van der Sloot [2001]. Hillier et al [1999] has argued that the tests to be used should be simple and inexpensive to set up and run, suitable for testing a large number of samples, and closely represent conditions encountered by concrete in the environment.

Van der Sloot [2004] have also shown that diffusion controlled release is related to the surface area of the specimen as well as the time of exposure. In the static monolithic leaching, or diffusion test a specimen (of regular geometry and known surface area e.g. a cube) is immersed in a volume of leachant solution. The leachant solution is sampled at defined intervals and replaced with fresh solution to accelerate the leaching rate. This test has the following advantages (Hoberg et al., 2000):

It is relevant to durable materials with a monolithic character (e.g. low permeability soil and sediments),
It is possible to identify the relative merits of solubility control versus dynamic leaching,
It is possible to isolate surface wash-off effects,
Determination of intrinsic release parameters is possible,
Allows reactive/transport modelling, and projection of long term behaviour is possible.

3.6.2 Tank leaching test for solidified specimen

After the batch leaching test was successfully carried out and the mobilized metals precipitated and tested, see section 3.4, it was necessary to develop further processes for remediation in order to stabilize the metals. To collect and retain them (in a suitable way such as a moulded cubic block) so that the necessary reactions will occur to achieve the main goal of stabilization and reduction of the leaching below a given threshold level. The solid-state specimen consisting of the OPC and metal solution was cured for different periods of time until it was set and retained its solid shape after the mould was removed, a process which required at least seven days.

Because both curing time and temperature play a role in the hydration reaction, it was necessary to take the room temperature into account, for these experiments the room temperature was $20C^0$. To investigate the release of the contaminant from the OPC block, a tank test was used in which the solid: liquid ratio (V/V) was 1:5. Hillier et al [1999] has argued that the tests to be used should be simple and inexpensive to set up and run, suitable for testing a large number of samples, and closely represent conditions encountered by concrete in the environment. To accommodate these suggestions and to attempt to minimise the time required to obtain the results the following protocol was used, see Tables 2.5 and 2.6 in chapter two.

The method adopted for the tank leaching test was essentially that as described by Van der Sloot, [2004] DD ENV 12920:2006+A1:2008, "Characterization of waste. Methodology for the determination of the leaching behaviour of waste under specified conditions". This updated British Standard document now accords with ANSI/ANS-16.1-2003;R2008 "Measurement of the leachability of solidified low-level radioactive wastes by a short-term test procedure". The standardized tank leaching tests that was used was the Netherlands Monolithic Leach Test (NEN 7345) [1995].

As the curing time plays a role in the hydration reaction and the integrity of the solidified sample, it was important when making the cubes of material for testing to consider the room temperature (which was 20°C) and humidity, and the period of time for which the cube would be immersed during each test. To investigate the release of the contaminant, the solid to liquid ratio was 1:5 S/L in the tank test.

It was found that if the cube was allowed to cure in the mould for only 1 day or 3 days, the cube fragmented after de-moulding. Therefore the cubes were kept in the mould for 7

days, which ensured that they remained solid after de-moulding and for the duration of the elution test.

The raw samples were measured using ICP (inductivity coupled plasma) for metals and NO_3^-, SO_4^{2-} and Cl^- by Ion Chromatography (IC), see Appendix 1. Measurement of concentration made by ICP for each tank were multiplied by 625 and divided by 150 (volume of leachant divided by the surface area of the cube) to give a result for leaching in terms of $\mu g/cm^2$.

3.6.3 Preparation of specimen and procedure for solidification

Curing is an essential part of the solidification process, and for this the metal solution and the stabilizing material were in placed in a plastic mould in the shape of a cube with sides 50mm, see Figures 2.1 and 2.2, and Section 2.3.3. All the moulds were kept at the same temperature and humidity to ensure uniform conditions for stabilization after adding OPC to the metal solution. The weight of dry OPC powder was measured at 200g, and 80ml of metal solution was added, so the ratio of the solution to OPC was 0.4 (W/C).that 80ml contain equivalent to 20,000mg/l of Pb which calculated for 20000mg/l*0.08 L, then 16000mg/1000 =1.6g of lead in each cube

The OPC was based on the dry weight. The metal solution was 20,000mg/l was prepared as described in Section 2.3.3, where the required amount of $Pb(NO_3)_2$ was added to 1 litre of DI water. The metal solution and OPC was mixed thoroughly using a plastic rod before the mixture was introduced to the plastic mould and left to set. Of course, metal hydroxides are amphoteric compounds and their solubilities will strongly depend on leachate pH level [Asavapisit, et al 2000]. Three separate tests were conducted simultaneously.

Major components of OPC are Al, Si, Ca, K, Mg and Na, see Table 3.3, and it was decided to measure these in addition to the contaminant element, Pb. The results for Pb are shown in Figure 3.24 which include the release rate and cumulative release rate for the contaminant.

3.6.4 Solidification and stabilisation of Pb in solution using OPC, tank leaching test

3.6.4.1 The Effect of curing on stabilising of Pb

The curing time of the stabilised and solidified (S/S) materials may have a large influence on their subsequent leaching behaviour. Because such physical properties as compressive

strength may vary with time, especially during the first months after the mixture preparation, some authors have recommended a curing time of 90 days to determine longer-term strengths and leachability of the material. Chaudhary [2004] has shown that as the curing time increased, the leaching rate of heavy metals from the solidified matrix reduces.

It should also be noted that the way samples are collected and stored can have a significant impact on the test results, particularly in the case of materials that present reducing conditions, such as sediments. Therefore, recommended procedures for sample storage should be followed. Chaia et al [2009] used only 7 days curing time and reported reduction of Cr leaching from OPC cube samples which is agreement with this study. Lombard et al., [1998] used 7 days for curing the sample and reported an 80% reduction for heavy metal leaching. The setting condition are important because temperature and air of affection on initial reaction rate Bentz [2002].

Shi and Fernandez [2006] reported that OPC-based binders have been widely used for S/S of wastes due to their low cost and ready availability. However, these binders are not very effective in stabilizing certain heavy metals including As, Cr, Cu, Hg and Pb. An alternative to OPC are alkali-activated cements, which have a number of environmental and economic advantages over traditional OPC. This suggested the procedure for preparing the specimens used in this study; adding NaOH to a Pb solution then mixing with dry OPC powder, resulting in stabilization of the Pb solution, see Section 2.3.4.

3.6.5 pH level of leaching fluid and Release of Lead during the OPC tank test

Figure 3.24 shows the leaching of Pb extracted in the renewable tank test for an OPC specimen. See Table 3.13 for the test data. The pH level of the leachant was monitored for each sample and showed that each time there was an increase in pH level there was a corresponding increase in Pb released, although the increase of pH as results of solubility of cement composition , see Figures 3.24 and 3.25. A drop of NaOH was added to the 80ml of contaminated solution to make its pH around 9 before it was added to the cement mixture which then will be cured in the mould for a period sufficiently long that it did not defragment on removal. An increase in pH level of leachate means that K, Na, Ca, etc., from the concrete leached out more readily.

The relation from this figures shows that pH increase is compatible with Pb release even with a pH above 12, as shown by the fact, over the 48 hour period from 24h to 72h the highest release of Pb was recorded, 2.58μg/cm^2.

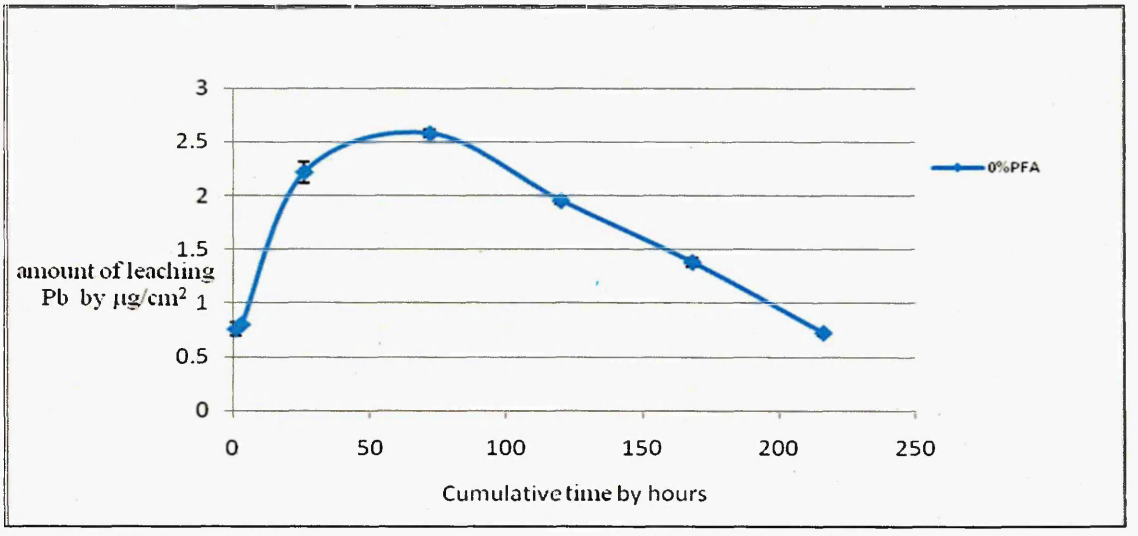

Figure 3.24 Cumulative Leaching of Pb (μg/cm^2) (n=3) as function of time in renewable tank leaching test (100% OPC +0%PFA cube)

Table 3.13 Leaching of Pb (renewable tank leaching test) for 100% OPC cubes

Total duration of immersion of OPC block in leachant (DI water) (hours)	Time between tests (duration of leachant in tank) (hours)	Tank 1 Pb mg/l	Tank 2 Pb mg/l	Tank 3 Pb mg/l	Mean (M) Pb mg/l	sd	Mean (M*625/150) (μg/ cm^2)	Mean (μg/ cm^2/hr)
1	*1*	0.220	0.226	0.210	0.217	0.062	0.90	0.90
3	*2*	0.174	0.204	0.199	0.192	0.016	0.80	0.40
24	*24*	0.48	0.683	0.440	0.534	0.130	2.25	0.11
72	*48*	0.588	0.660	0.610	0.619	0.036	2.58	0.05
120	*72*	0.438	0.499	0.470	0.469	0.030	1.95	0.04
168	*96*	0.300	0.377	0.320	0.332	0.039	1.33	0.03
216	*120*	0.135	0.211	0.177	0.174	0.038	0.73	0.02
Total lead leached out		1.58 x10^{-3} g			2.53 mg/l		10.5μg/cm^2	

It can be seen from the above table that in this study the total release of Pb in the tank test after 120h was 10.42μg/cm^2, equivalent to 1.56 x10^{-3}g(2.53*625/1000*10^{-3}). Because the time intervals were not equal the maximum leached out in any one interval was 2.58μg/cm^2 for the period between 24h and 72h. For the final 48 hour period, from 168h to

216h the amount leached out was 0.73μg/cm^2. As would be expected the hourly rates were a maximum at the beginning and then fell away quite sharply, see Table 3.13.

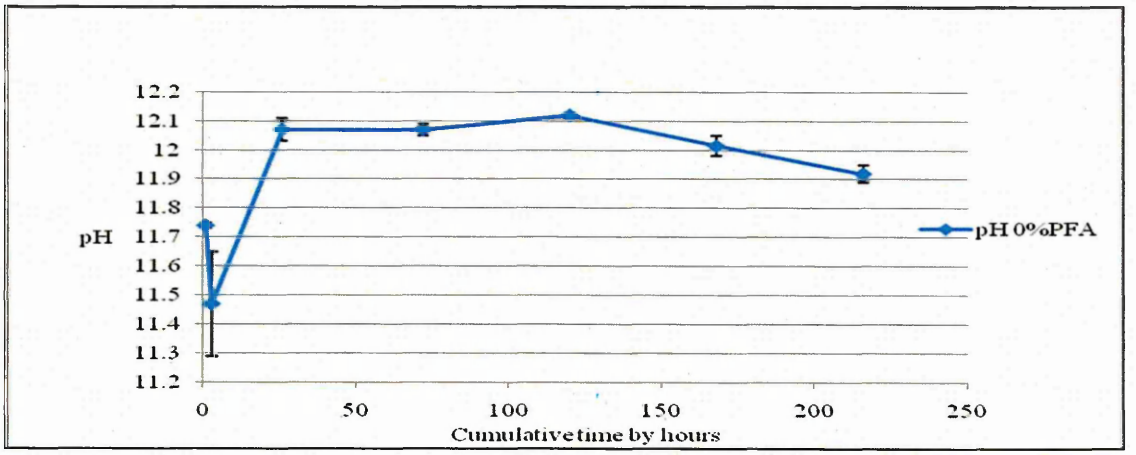

Figure 3.25 pH level as a function of time (renewable tank leaching test,(100% OPC+0%PFA or 0%GGBFS ,50mm cube)

Table 3.14 pH levels of leachant measured at end of each period of immersion (renewable tank leaching test; leaching Pb from 100% OPC 50mm cubes)

Total duration of immersion of OPC block in leachant (DI water) (hours)	Time between tests (duration of leachant in tank) (hours)	pH Tank1 at end of leaching period	pH Tank2 at end of leaching period	pH Tank3 at end of leaching period	Mean pH	sd
1	*1*	11.75	11.73	11.74	11.74	0.01
3	*2*	11.65	11.29	11.47	11.47	0.18
24	*24*	12.03	12.12	12.07	12.07	0.04
72	*48*	12.05	12.09	12.07	12.07	0.02
120	*72*	12.13	12.11	12.12	12.12	0.01
168	*96*	12.05	11.98	12.01	12.02	0.04
216	*120*	11.89	11.95	11.92	11.92	0.03

Sd=standard deviation

Marion et al [2005] has reported that, regardless of the cement type, the release of heavy metals into the leachate falls sharply with increase in duration of immersion, when normalized to release per 24h, and this has been confirmed here. This occurred despite periodic renewal of the DI water, which provided the possibility of increased leaching activity. This means that for most heavy metals, leaching becomes insignificant after lengthy immersion.

Odriozola and Gutie [2008] Fick's diffusion theory as standardized by ANS(ANS, 1986) can provide a model to determine the cumulative fraction of Pb leached with time because the leaching of the contaminant from cement-based waste forms is a process largely controlled by diffusion.

Moon and Dimitris [2006] have suggested that the slow rate of diffusion of contaminants allows the assumption that a quicklime-based waste form is a semi-infinite medium due to presence of CaO, much like the cement-based waste forms examined in previous studies of has high composition of CaO. Both Andrés et al [1995] and Marion et al [2005] have claimed that this type of behaviour supports a model of leaching for concrete in a tank test where the leaching rate would be proportional to the square root of the duration of the leaching. Unfortunately, real field conditions will usually differ significantly from those in a tank test. With natural exposure, the concrete will be exposed to an unknown and possibly unlimited water volume and the solubility conditions will vary according to an unknown pH level. In this study the pH of release were increased by time until reached to the peak at 72h.

Alpaslan and Yukselen [2002] have described how the solubility of lead hydroxide $Pb(OH_2)$ increases with solubility from a minimum value at pH level of about 9.5 to a significantly greater value for pH values >11. These authors suggest that the mechanism responsible for the decrease in the amount of leached lead in the pH range of 12.5–13 is not only due to the precipitation $Pb(OH)_2$ but also entrapment of lead in the crystal structures of the cementitious compounds formed as a result of pozzolanic reactions. In this study the decrease occurred at 11.47 and 11.92, see Figures 3.24 and 3. 25.

The results of Diet et al [1998] agree with this trend of results of movement of pH curve against cumulative time, see Table 3.14 and 3,13 in this study and also Figures 3.24 and 3. 25. Diet et al [1998] also reported that the flow of $Ca(OH)_2$ through the sample surface had some control over the leaching behaviour because alkali ions have a small influence on the final pH level of the leachate. The pH level appeared to be controlled by the leaching of NaOH and KOH, and the presence of ettringite which, in the presence of water, sulphate and calcium ions, released alkalis which increase the pH level of the solution.

3.6.6 Release of Calcium during the OPC tank test

With cement-based materials, calcium hydroxide ($Ca(OH)_2$) is primarily responsible for calcium release. The $Ca(OH)_2$ occurs in the form of portlandite, and as this nears depletion,

the CSH controls calcium solubility. The solid lead speciation is not known, it may be incorporated in CSH or as PbO or $PbCO_3$ as shown by XRD results. When the OPC cube is immersed in water, the dissolution precipitation processes begin at the solid/pore/water interface together with chemical reactions in the aqueous phase. Simultaneously, because of the concentration gradients that exist in the solutions within the pores of the material, chemical species migrate from within the material to its surface and will appear in the eluate. This phenomenon shows that the contact time between leachant and material is not the only important factor involving the liquid phase, the hydrodynamics of the liquid phase can also be important for element depletion in the material, as will be saturation level of the eluate [Barna et al 2004].

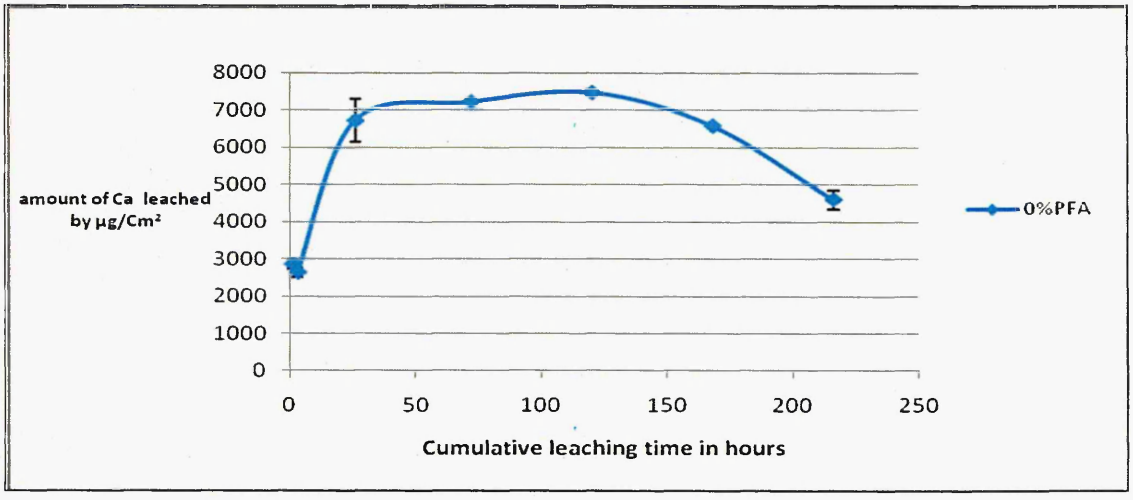

Figure 3.26 Cumulative leaching of Ca (µg/cm^2) (n=3) as a function of time in renewable tank leaching test (100% OPC+0%PFA, 50mm cube)

Figures 3.26 and Table 3.15 show data gathered for the release of Ca during the tank leach test. As can be seen the amount of Ca leached out in the first hour is 2847µg/cm^2, and in the period from one to three hours is 2634µg/cm^2 after which time the rate of extraction fell quite sharply and then gradually levelled off. Because of the time intervals for which the readings were taken were not equal the measured calcium extracted reached a peak of about 7482µg/cm^2 for the period between 72h and 120h. For the 48 hour period between 168h and 216h it was 4601µg/cm^2. The same pattern is observed as for the extraction of Pb, Figure 3.24.

Table 3.15 Cumulative release of Calcium at varied time (renewable tank leaching test) for 100% OPC +0%PFA or 0%GGBFs) 50mm cubes

Total duration of immersion of OPC block in leachant (DI water) (hours)	Time between tests (duration of leachant in tank) (hours)	Tank 1 Ca (mg/l)	Tank 2 Ca (mg/l)	Tank 3 Ca (mg/l)	Mean Ca (mg/l)	sd	Mean Ca ($\mu g/cm^2$)	Mean Ca ($\mu g/cm^2/h$)
1	*1*	583	784	683	683.4	100	2847	2847
3	*2*	514	750	632	632.1	118	2634	1317
24	*21*	1028	2197	1613	1613	584	6720	320
72	*48*	1655	1814	1735	1735	79.4	7228	151
120	*48*	1715	1876	1796	1796	80.6	7482	156
168	*48*	1578	1582	1580	1580	1.90	6584	137
216	*48*	852	1357	1104	1104	252	4601	96
Total Ca leached out		5.714.3 g			9143		38095.8	

3.6.7 Sodium and potassium release during the OPC tank leaching test

The main alkalis present in all Portland cements are Na and K, and for many purposes an upper limit is placed on the allowable total equivalent alkali content. Much research has been conducted (see, for example, Liu et al [2005]) into the influence of Na and K on cement microstructure, hydration and performance. Bentz [2005] has reported that the presence of alkalis modify the morphology of the calcium silicate hydrate gel (C-S-H) by producing a more alkalis hydration product (Na, K).

The release of Na was measured using ICP; see Figures 3.27and Table 4 in the appendix. The pattern of the release of Na is very similar to those of Pb and Ca. The amount of Na released in the first hour was 43.8$\mu g/cm^2$. This fell to 32.4$\mu g/cm^2$ over the period 1h to 3h, after which there was a further drop. The average release of Na over the interval from 24h to 72h, was 2.8$\mu g/cm^2$/hr and at the end of the test, in the period 168hto at 216h, the release rate was down to 2.0$\mu g/cm^2$/hr. Because of the time intervals at which the readings were taken there is a maximum at 72h in Figure 3. 27

Figure 3.28 and Table 5 in appendix **1(Table A1 8.5)** shows the pattern of the release of K is very similar to those of Pb, Ca and Na. The amount of K released in the first hour was 265ug/cm^2. This fell to 182ug/cm^2 for the time interval between 1 and 3 hours, after which

there was a sharp drop. The average release of Na the interval from 2 to 24h, was 27.2μg/cm^2/hr and at the end of the test, in the period 168h to at 216h, the average release rate was down to 8.0μg/cm^2/hr. Because of the time intervals at which the readings were taken there is a maximum at 24h in Figure 3. 28.

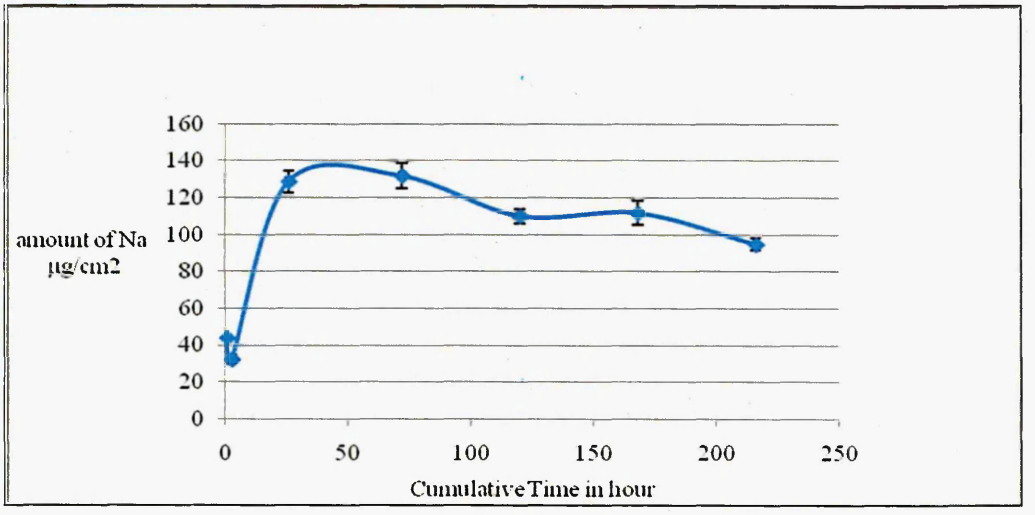

Figure 3.27 Cumulative leaching of Na (μg/cm^2) as a function of time in renewable tank leaching test (100% OPC cube),(n=3)

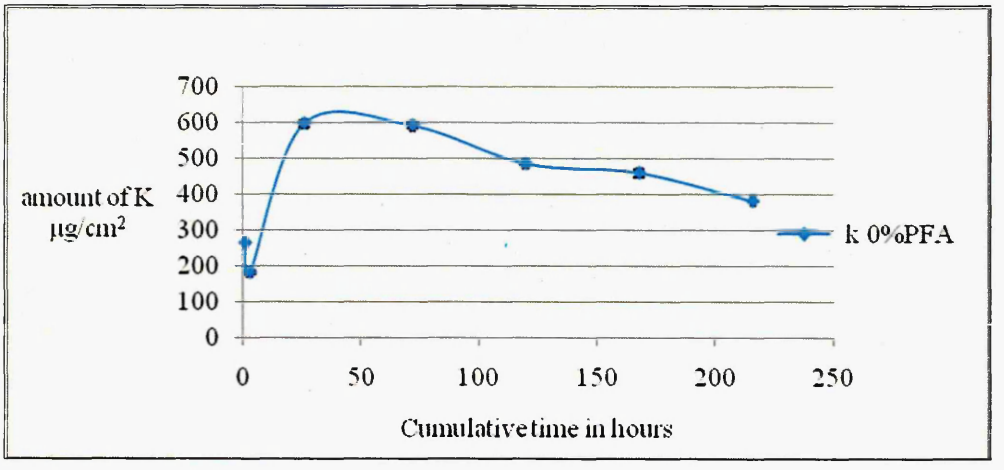

Figure 3.28 Cumulative release of K (μg/cm^2) (n=3) as a function of time in renewable tank leaching test (100% OPC cube)

The amount of Na and K released is due to the reaction between the cement and water. The cement released relatively large amounts of Na and K which provides the alkalinity that increased the pH value. Sanchez et al [2003a] supported the trend of the results of this study.

3.6.8The release of Al during the OPC tank test

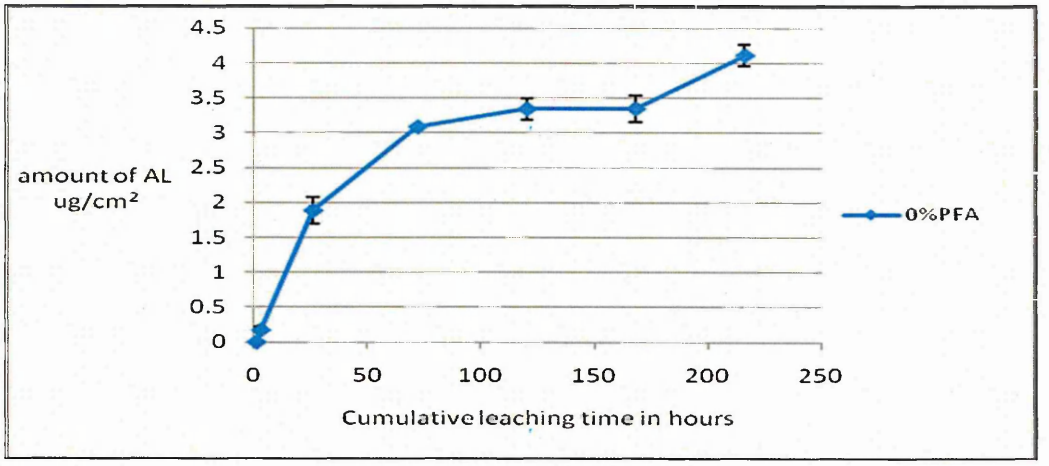

Figure 3.29 Cumulative release of Al ($\mu g/cm^2$)(n=3) as a function of time in renewable tank leaching test (100% OPC cube)

The release of Al were measured by ICP, the composition of OPC has 4.8 % of Al_2O_3, see Table 3.3. Because of the time intervals over which the measurements were taken the leaching of aluminium appears to be very low at 1h and then it rises to 0.17$\mu g/cm^2$ over the period 1h to 3h, after which it appears to continues to increase and reaches a peak of 4.13$\mu g/cm^2$ for the period 168h to 216h, See Figure 3.29 and Table 6 in appendix and The rate of leaching release the maximum in the first hour, after which it falls and then begins to rise again.

3.6.9The release of chlorine during the OPC tank test

As can be seen from Fig.3.30 and Table 7 in appendix, the highest release was 3.09$\mu g/cm^2$ measured at 1h. The measurements dropped sharply at the 3h reading to less than 0.4$\mu g/cm^2$, and by 168h the hourly rate had fallen to nearly zero. Zhu et al [2007] have reported and that the type of cement used will determine the limited ability of the cement to chemically react with chloride and that the ratio of water to cement is a primary determinant of the chloride ion critical content, For example, sulphate resisting cement with a low C3A content is less able to react with chlorides. In this study, the type of cement was OPC and this explains the results obtained here because OPC contains no Cl , a result which is in agreement with the American Concrete Institute .Grace & Conn [2009]. The apparent negative reading for Cl seen in the figure shows no free Cl was detected in

the sample, However, the large decrease in the relase of Cl could be taklen as an indication that OPC is long term resistant to the corrsion which may be caused by Cl.

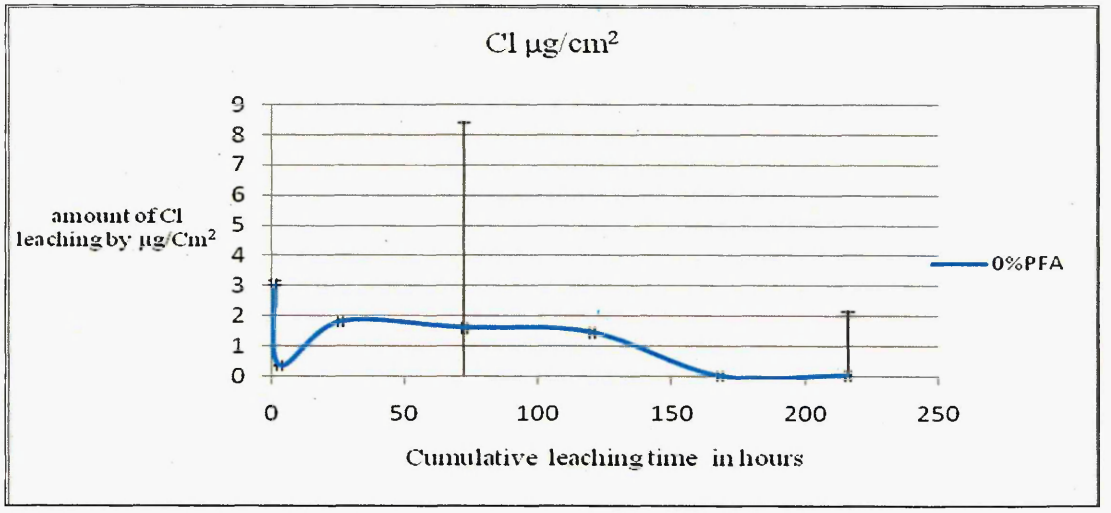

Figure 3.30 Cumulative leaching of Cl (µg/cm^2) (n=3) as a function of time in renewable tank leaching test (100% OPC cube)

3.6.10 The release of sulphates during the OPC tank test

As can be seen from Figure 3.31and Table 8 in appendix 1 the highest release was 38.3µg/cm^2 measured at 1h. The measurements dropped sharply at the 3h reading to 3.24µg/cm^2 and by the end of the test (216h) the hourly rate had fallen to 0.11ug/cm2/h. Interestingly, there appears to be a broad minor peak in release of SO_4^{2-} which extends over the period from about 72h to 168h. This appears to be maximum because the measurement of 12.0µg/cm^2 at 120h is significantly greater (at the 95% confidence level) than either the 7.44 µg/cm^2 measured at 72h or the 7.33µg/cm^2 measured at 168h. No reason for this peak comes to mind and for the present is attributed to a shift in IC calibration. Berrymana et al [2005] reported sulphate behaviour is determined by the ettringite existing for pH>10 and gypsum for pH<7. Between these pH limits the concentration is limited by the available quantity of sulphate

Sulphate originates from the dissolution of gypsum which is added to the cement clinker to control hydration of the tricalcium aluminate (GA) phase. The reduction in concentration is due to SO_4^{2-} combining with the aluminate phases, to form insoluble ettringite or sulpho-aluminate gel. After 120 hours the SO_4^{2-} ions have disappeared from solution see Figure 3.

31. Asavapisit and Cheeseman [1997] are in agreement with this trend of results and have also reported that the presence of Pb delayed the removal of SO_4^{2-} from the leaching solution.

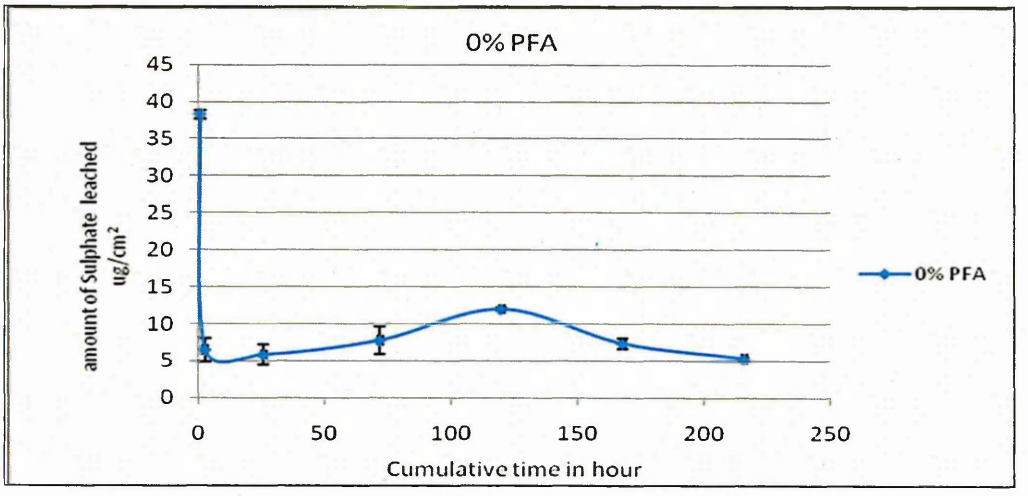

Figure 3.31 Cumulative leaching of sulphate (µg/cm$^{2)}$ (n=3) as a function of time in renewable tank leaching test (100% OPC cube)

3.6.11 The release of nitrates during the OPC tank test

The releases of nitrates NO_3^- were measured by IC in a similar procedure to the measurement of sulphate and chlorine. As can be seen from Fig. 3.32 and Table 9 in appendix, the highest release was 55.6µg/cm^2 measured after the first hour. The measurement for the period from 1h to 3h was 26.3µg/cm^2 (an hourly rate of 13.2µg/cm^2/h) and by end of the test at 216 h, the hourly rate had fallen to 2.4µg/cm^2/h. interestingly, there appears to be a broad minor peak in release of NO_3 which extends over the period from about 72h to 168h. As with the SO_4^{2-} this also appears to be a real peak in the sense that the measurement at 120h is significantly greater (at the 95% confidence level) than the measurements made at either 72h or 168h. The release of NO_3 was higher than either SO_4^{2-} or Cl^- due to the presence of NO_3^- in the form of $Pb(NO_3)_2$, introduced in contaminant solution, see Chapter 2. The peak at 120h and the small rate of decline of the hourly leaching rate indicate the amount of NO_3^- that remains bound in the OPC cube.

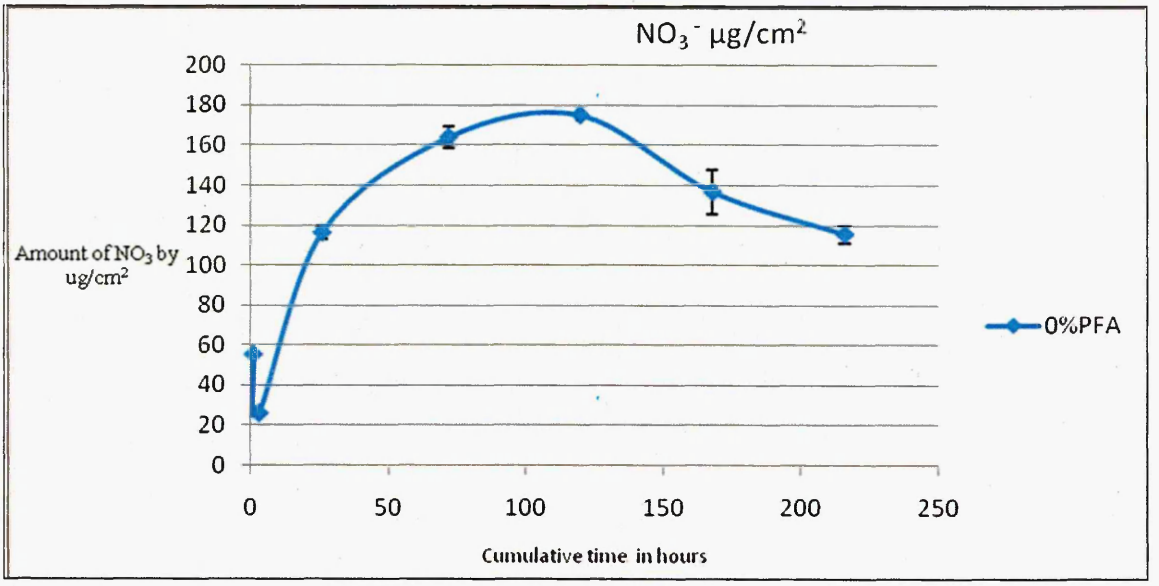

Figure 3.32 Cumulative release of Nitrate (µg/cm^2)(n=3) as a function of time in renewable tank leaching test (100% OPC +0% PFA or 0% GGBFS 50mm cube)

3.6.12 The acid extraction test

Digestion tests were performed to determine how much available contaminant is in the samples. Here samples (OPC stabilized Pb) of mass 0.5g, that will dissolve in the acid with heating for 10 or 30min The availability of the contaminant was identified by acid digestion test for 1 g of OPC, (see 2.2.4) and using XRF before and after immersing the specimen in the tank.

The amount of 0.5g of OPC which extracted 1318 µg/g then multiple it on 2 times to be in 1g 2636 µg/g and the average of weight of the sample is 200 g wet powder of OPC , see Section 2.2.4. Table 3.16 shows the maximum extractions were achieved.

Table 3.16 Acid digestion test for the OPC with Pb, 30 min duration. Vol.25

sample	mg/l	mass of lead leached out (µg/g)	5ml acid
1	53.91	1348	HNO_3
2	54.89	1372	
3	54.23	1356	
4	49.02	1226	
5	51.71	1293	
6	48.35	1209	
Mean	543	1319	
sd		0.5	

Chapter Four

Effect of lime on metal contaminated soils and solutions

4.1 Methods for measurement of the leachibility of lead

The soils and level of lead contamination used to investigate the effect of adding lime were the same on those used in the previous chapter, as described in chapter two sections. 2.2.4.

The maximum leaching out of lead 780μg/g was obtained using acid digestion .The test is described in Chapter Two ,see 2.2.4, and the results in chapter three Table 3.1.

4.2 Effect of Lime on metal contaminated soils and solution

In this chapter the raw materials were analysed using X -ray fluorescence spectroscopy (XRF). Table 4.1 shows the chemical composition for soil and lime used in this study which is the same soils were described in Chapter 2, section 2.2.1 and 3, obviously the major content of the lime is CaO, which is about 60 %.

Table 4.1 The chemical composition (by mass%) for lime and uncontaminated soil

Component	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	Mn_3O_4	Fe_2O_3	ZnO	SrO	BaO
Hydrated lime	0.13	0.22	0.13	0.83	0.04	0.09	ND	60.1	0.01	0.05	0.05	0.01	0.07	0.01
Uncontaminated soil	0.20	0.13	2.89	93.6	0.02	0.06	1.72	0.12	0.08	0.01	0.65	0.01	ND	0.03

Previous experiments showed that pH is an important factor for the remediation process. Lime can be used as an additive to increase the pH level, therefore it was necessary to examine the use of lime to immobilize the Pb in solution the addition of 0.1 g of lime to 50 ml of DI water resulted in an increase of pH to 11.9. The measurement was replicated with only 0.01 sd, the pH of deionised water is 5.4.

4.2.1 Effect of lime on lead solution

In Table 4.2 the effect of 0.1 g of lime on the lead solution was obvious in reducing the concentration of lead in the eluted solution. The investigation of the effect of lime on the lead solution was carried out for five different concentrations of lead solution, 10, 50, 100, 500, 1000 mg/l, see Table 4.2, 4.3, and 4.4. The results show the effect of mixing the lime powder with 500mg/l of Pb solution. The reduction in concentration of lead in the solution was 90%. The results for the 1000mg/l solution of lead are shown in Table 4.5.

Table 4.2 Effect of 0.1g of lime on lead solutions of concentration 10mg/l and 50mg/l

Sample	Pb (mg/l)	Mean	Sd	pH	Mean of pH value
10mg/l of lead solution + 0.1 g of hydrated lime	0.7			9.2	
10mg/l of lead solution + 0.1 g of hydrated lime	0.7	0.7	0.0	9.3	9.2
10mg/l of lead solution + 0.1 g of hydrated lime	0.7			9.3	
50 mg/ of lead solution + 0.1 g of hydrated lime	1.1			11.8	
50 mg/l of lead solution + 0.1 g of hydrated lime	0.8	1.05	0.24	11.6	11.8
50 mg/ of lead solution + 0.1 g of hydrated lime	1.3			11.8	
Measured concentration of 50 mg/l of lead solution	50.7			2.8	
Measured concentration of 50 mg/l of lead solution	49.4			2.8	2.7
Measured concentration of 50 mg/l of lead solution	49.4			2.6	
Measured concentration of 10 mg/l of lead solution	10			2.6	
Measured concentration of 10 mg/l of lead solution	9.7	9.81	0.01	2.7	2.65
Measured concentration of 10 mg/l of lead solution	9.8			2..6	

Sd=standard deviation

The pH of the sample with 10 mg/l Pb is 9.2 due to a present of acid in the lead solution, since the solution were made from a stock of standard lead solution used usually to prepare the calibration solution of ICP. The effect were obvious on the final solution where n o lead was found in the elute after filtration by 542 Whatman paper, also an increase in the pH to 11.8, at low Pb concentration 10mg/l and 50 mg/l ,the lime removed the lead by almost 99.9% at 100 , 500 mg/l and 1000 mg/l the lime removed the lead from the solution to 90%.

Table 4.3 Effect of 0.1g of lime on 100mg/l and 500mg/l lead solutions

Sample	Pb (mg/l)	pH
500mg/l of lead solution + 0.1 g of hydrated lime	56.9	12.1
500mg/l of lead solution + 0.1 g of hydrated lime	55.9	12.2
500mg/l of lead solution + 0.1 g of hydrated lime	45.9	12.1
Mean	52.9	
sd	6.0	
100 mg/l lead solution +0.1 g of hydrated lime	4.5	12.3
100 mg/l of lead solution + 0.1 g of hydrated lime	7.6	12.3
100 mg/l lead solution + 0.1 g of hydrated lime	5.9	12.3
Mean	6	
sd	1,5	
Measured concentration of 500 mg/l of lead solution	494	4.0
Measured concentration of 500 mg/l of lead solution	491	3.7
Measured concentration of 500 mg/l of lead solution	493	3.6
Mean	493	
sd	1.52	
Measured concentration of 100mg/l of lead solution	99	3.9
Measured concentration of 100mg/l of lead solution	97	3.8
Measured concentration of 100mg/l of lead solution	100	4
Mean	98.6	
sd	1.05	0.07

Table 4.4 Summary of effects of 0.1g of lime on different concentrations of lead solution

Sample	1000 mg/l + 0.1 g of lime	500 mg/l + 0.1g of lime	100 mg/l + 0.1 g of lime	50 mg/l + 0.1 g of lime	10 mg/l + 0.1g of lime	DI water + 0.1g of lime	De-ionised water
mg/l of lead in leachant solution	100.3	52.9	6	1.05	0.7	0.82	0.73
Amount of reduction %	90	93	94	98	93	-	-
pH	12.2	12.1	12.3	11.7	11.3	12	5.6

Table 4.5 Effect of 0.1g of lime on a 1000mg/l solution of lead and amounts of elements and anions Cl^-, NO_3^-, and SO_4^{2-} released as a consequence

Sample	Pb (mg/l)	Mg (mg/l)	Ca (mg/l)	Na (mg/l)	K (mg/l)	Cl^- (mg/l)	NO_3^- (mg/l)	SO_4^{2-} (mg/l)
0.1g lime + 1000 mg/l of lead solution	116	ND	4414	2.27	0.068	1.19	1198	5.2
0.1g lime + 1000 mg/l of lead solution	89	ND	4578	1.45	0.047	1.02	1106	5.07
0.1g lime + 1000 mg/l of lead solution	96.1	ND	4954	1.41	ND	1.02	1929	4.85
Mean	100.3	ND	4649	1.71	0.038	1.08	1411	5.06
sd	13	ND	276	0.48	0.014	0.09	450	0.17

ND: non detected

While measuring the effect of lime on the Pb solution, the amounts of other elements of interest (Ca, Na, K and Mg) which were released in the leachant were determined, as were the anions Cl, NO_3 and SO_4. The addition of lime reduced the concentration of the lead contaminant in solution by about 90% although the standard deviation was +/- 13 and as consequence of adding the lime there was a release of associated elements Mg, Ca, K, Na. The concentrations of these in the leachant were measured. It was observed that a large amount of Ca was released 4954 mg/l which is about 5 times the level lead in the blank solution, but in addition 1.7 mg/l of Na was also leached out of the treated samples, see Table 4.5.

The other constituents which were measured were: Cl^-, NO_3^- and SO_4^{2-} Substantially more nitrates were released than Cl^- and SO_4^{2-}, see Table 4.5. The high amounts of NO_3 in the

samples were due to the $PbNO_3$ salts and because the solubility of NO_3^- is high as result of the increase in pH level due to the addition of lime.

An acid wash (0.001M HNO_3) was used on the filter and glassware after conducting the leaching tests. The concentration of lead in the wash solution increased, which demonstrates that lead was precipitated, and remained, on the surface of the filter and the glassware,which is about 75% of the lead formed on the surface. This helps answer the question of where the lead was formed since it was not detected using ICP on the final solution of leaching test.

Precipitation reactions were investigated by collecting material on the surface and dissolved in acid wash. The findings of Chen et al., [2009] in their study, which examined the effects of lime on contaminated aqua solution, are in agreement with this study that precipitation occurred as a result of adding lime to metals in solution.

4.2.2 Effect of lime on a solution contaminated with a mixture of metals

The amount of nitrate salts required for solution of each element was the amount required for a 1000mg/l concentration of the solution. (see chapter 2).

The effects of lime on mixture of metals were tested in the same way of treating the lead solution. The reduction were 99.9 % Pb, Cr, Al, Cu, Fe, but lower for Ni, which was 80 % , Cd for 55 % and 92 % for Zn. Table 4.7 represents those measurement taken by ICP for each element in µg/g ,some samples were below the detection limit of the ICP(N/D). The Zinc was not detected and is not represented in Table 4.6.

In Table 4.7 iron was included and detected in the metal mixture. The effect of lime was almost 99 % reduction in concentration of metals in mixture solution, except for Cd which was 55 % and Ni about 80% , the zinc was 95%, the pH was 6.9. The difference in the two Tables are presented of Iron elements in the solution and final pH ,see Table 4.7. The pH was 6.9, no detection that indicates negative were for Pb, Cr, Al, Cu and Fe, which was not represented in Table 4.7.

Table 4.6 Effect of lime on a mixture of heavy metals (Pb, Ni, Cd, Cr, Al, Cu, and Zn) in solution containing 100mg/l of each element

Sample	pH	Pb (mg/l)	Ni (mg/l)	Cd (mg/l)	Cr (mg/l)	Al (mg/l)	Cu (mg/l)	Mg (mg/l)	Ca (mg/l)	Na (mg/l)	K (mg/l)
0.1g of lime+100mg/l of Mixture	7.4	0.12	0.212	0.51	0.35	0.15	0.28	0.143	629.1	0.56	0.23
0.1g lime+100mg/l of Mixture	7.4	0.12	0.214	0.99	0.36	0.002	0.297	0.69	656.2	0.79	0.35
0.1 g lime+100mg/l of Mixture	7.6	0.115	0.208	0.44	0.36	0.43	0.281	0.028	708.3	0.72	0.05
Mean	7.4	0.004	0.211	0.65	0.36	0.21	0.28	0.28	664.5	0.67	0.21
Sd	0.1	0.002	0.003	0.3	0.001	0.24	0.009	0.35	40.2	0.12	0.15

Table 4.7 Effect of 0.1 g of lime on mixtures of heavy metal solution(Zn, Pb, Ni, Cd, Cr, Al, Cu and Fe) in solution containing 100mg/l of each element

Sample	pH	Zn (mg/l)	Ni (mg/)l	Cd (mg/l)	Mg (mg/l)	Ca (mg/l)	Na (mg/l)	K (mg/l)
0.1g Lime+100mg/l of metal solution	6.9	4.51	12.2	38.9	0.38	675.9	0.26	0.27
0.1g of Lim+100 mg/l of metal solution	7.0	11.6	23.12	56.97	0.36	659.0	0.28	0.22
0.1g of Lime+100mg/l of metal solution	7.1	8.08	18.76	46.8	0.37	667.2	0.56	0.79
Mean	6.9	8.06	18.02	47.5	0.37	667.4	0.37	0.42
Sd	0.09	3.54	5.49	9.01	0.01	8.4	0.16	0.316

Nd :No detection of Pb,Cr, AL,Cu and Fe,

4.2.3 The Effect of adding hydrated lime to lead contaminated soils

The trials began with the addition of a small amount of lime to the lead contaminated soil which is 0.25 g that equivalent to 0.5 % of contaminated soil. The quantity of lime was gradually increased until maximum reduction was reached, which was 99%, see Figures 4.1, 4.2 and 4.3. Also in Table (4.8) the 0.5% were calculated according to leaching batch test with a S/L ratio of 1:10, with two hours leaching with the shaker platform set to a constant rotary speed of 300r.p.m, the soils was 5 g of contaminated soil and 50 ml of deionised water.

Figure 4.1 and Table 4.8 shows that an increase in the amount of lime has affected the leaching rate of the lead from contaminated soil using 0.1 g of lime, which was equivalent to 2% total weight of solid, the reduction of lead was about 95 % as in Table 4.8.

Addition 0.1g of lime to 5 g of lead contaminated soils shows a great effect of lime on reduction of contamination in soil with pH above 11, as seen in Table 4.9 and Figures 4.1 and 4.2. In the acid wash most of the lead was bound to the surface of the filter and glass. This lead was dissolved by using acid wash that contained 10% of Nitric acid and 50 ml of deionised water. The release of lead by the shaking test, using deionised water as leaching fluid, with adding 0.1 g of lime to 5 g of lead contaminated soil, a greater amount of lime shows the lead were bound and that there is little release of lead, to only around 5 μg/g, which is much less than from the samples not treated with lime.

The vertical axis in Fig. 4.2 represents . the amount of leaching of Pb in mass μg/g, the last two bars show the contaminated soils treated with 1 % and 2% lime, the acid wash sample it means the what could not be leached out by deionised water , the acid solution of 10 % was used to wash the filter and beakers . The optimum amount of lime used was 2 % of total weight of soils was sufficient to reduce the lead in the final solution by 98 % by using deionised water as leaching fluid (see Table 4.8 and Fig.4.1 and 4.2).

Table 4.8 Effect of lime on lead contaminated soil and acid wash on precipitation of lead on surface

Sample	Lead (mg/l)	Lead (µg/g)	pH
contaminated soil + 50 ml DI water	4.7	47	4.6
contaminated soil + 50 ml DI water	4.87	48.7	5.3
contaminated soil + 50 ml DI water	3.19	31.9	4.5
Mean	4.2	42.53	4.8
sd	0.92		0.435
acid washing of contaminated soil	7.75	77.5	
acid washing of contaminated soil	7.81	78.1	
acid washing of contaminated soil	7.31	73.1	
Mean	7.62	76.23	
sd			
contaminated soil+ 0.1 g of lime+ 50 ml of DI water	0.323	3.23	12.1
contaminated soil+ 0.1g of lime +50ml DI water	0.772	7.72	12.1
contaminated soil + of 0.1 g of lime+ 50ml DI water	1.04	10.4	12
Mean	0.71	7.11	12.0
Sd	0.36		0.057
acid washing			
contaminated soil + 0.1 g lime	60.56	605.6	
contaminated soil + 0.1g lime	61.2	612	
contaminated soil+ 0.1 g lime	59.7	597	
Mean	60.48	604.8	
sd	0.7	7.5	

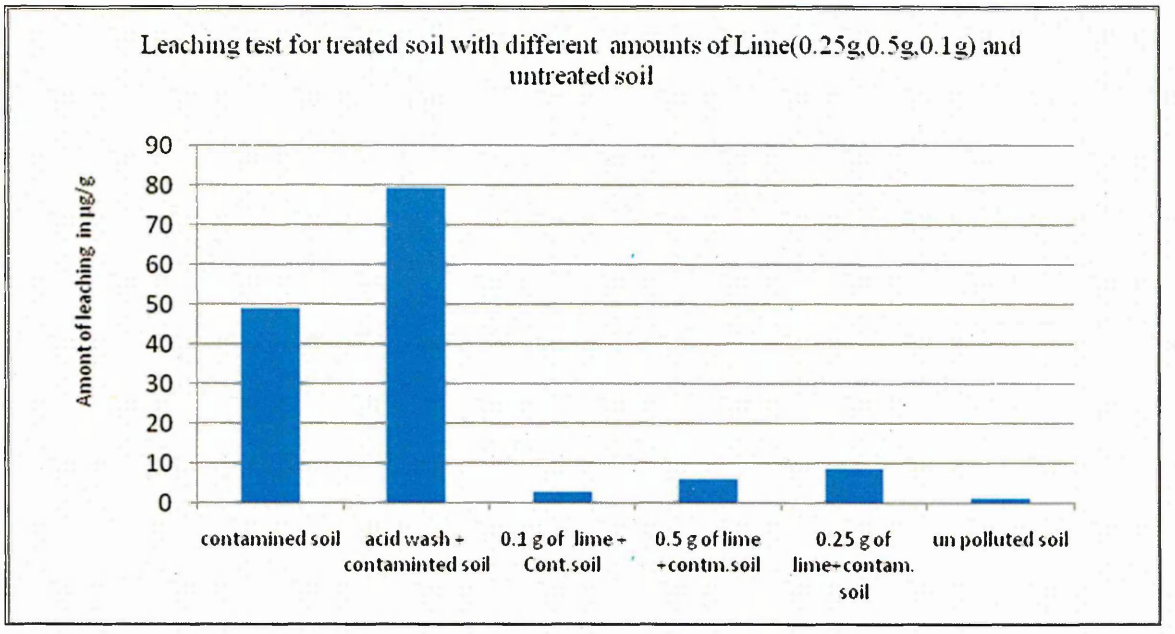

Figure 4.1 The effect of varied amount of lime on 5 g of lead contaminted soil. leaching fluids 50ml of DI water and the effect of 50 ml of acid wash on 5 g of lead contminated soil

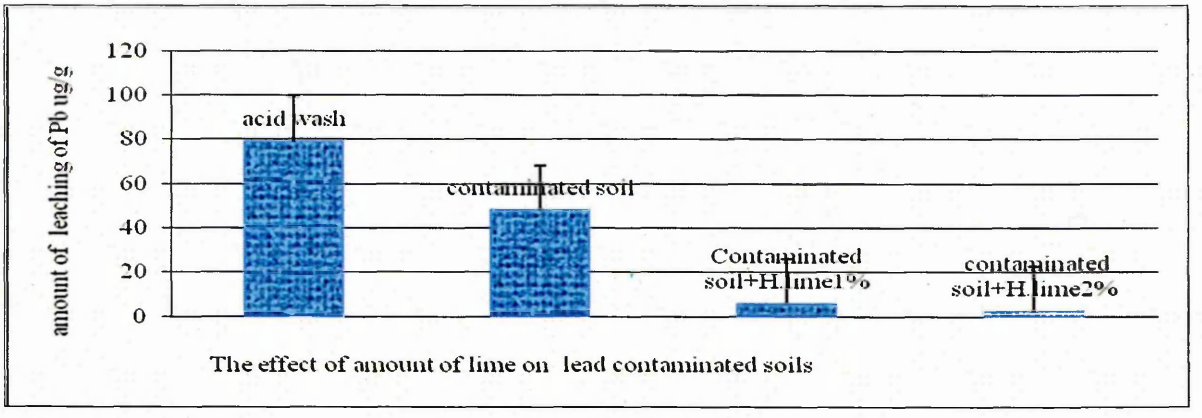

Figure 4.2 Effect of 1% and 2% of lime on 5 g of lead contaminated soil, leached by 50 ml of DI water and the effect of acid wash on precipitated material.

Yukselen and Alpaslan [2001] using a 1/15 ratio , lime to soil, with TLCP (toxicity leaching characterization procedure) test, found a reduction in leaching both Cu and Fe, 90 % Cu and 94 % of Fe, which is in a agreement with trend of results in this study, that 98 % reduction in Pb in final solution was reached using 0.1 g of lime additive to 5 g of contaminated soil.

Also, Boardman [1998] reported that 2.5 % of quick lime was sufficient to remediate the lead in clay soil (china clay) and also used 7% lime to remediate the iron metal contaminated clay soils. The additions of lime were applied in the aqueous phase of metals solution which caused an increase of pH of the metal solution, a conclusion in agreement with this study.

4.2.4 Effect of type of leaching fluid on lead contaminated soils and lime treated soils

The effect of lime on contaminated soils was investigated using different leaching fluids, deionised water, 0.1 M HNO_3 and 0.01M HNO_3. The reduction of lead in the final treated soil using deionised water as leaching fluid were 100 % compared with 38 μg/g in untreated soils, the pH in the final solution rose to 12.4 from 5.4. The release of Ca was 4000 μg/g while in untreated soil it was 180 μg/g. Na and K release were 22 and 82 μg/g respectively in untreated soil was 5.4 μg/g and 17 respectively also no release of Mg was detected in treated soils while in contaminated soils it was 19μg/g .

Using 0.01 M HNO_3 as leaching fluid the reduction in lead in the final solution was 3.2 μg/g, which is 98 % of the original from untreated soil 744 μg/g, the pH rose to 11.9 from 2.2 , the increase in the Ca release were 22000 μg/g, from 2400 μg/g in untreated soils, the release of Mg were 270,there was not any detectable release of Mg on adding lime. No increase on release Na and K, while in contaminated soil there was 4 and 19.6 μg/g, respectively.

Using 0.1M HNO_3, which has pH 1.2 as leaching fluid, in treated soil the release was 711 μg/g compared with untreated soils where it was 858 μg/g, the reduction was only 18 % lead in the final solution, there was not any detectable of increase in the pH in the final solution. Ca was 51000 μg/g compared with contaminated soils was 2600 μg/g, Mg release was 320 μg/g in untreated soil was 280 μg/g, large increases in Na and K, 37 and 102 μg/g respectively while in untreated soil it was 5 μg/g and 21μg/g respectively .

Lime was very effective as a stabilizer material in reducing lead leaching with using 0.01 M HNO_3 or deionised water as leaching fluid solution. Lime is not so effective when using 0.1M HNO_3 solution. (See Table 4.9).

Table 4.9 Effect of lime on lead contaminated soil with different leaching fluid

Leaching fluid (50ml)	Sample	pH of final solution	Pb (µg/g)	Ca (µg/g)	Mg (µg/g)	Na (µg/g)	K (µg/g)
De-ionised water	5 g Contaminated soil	5.4	37.6	180	19	5.4	17
	0.1g Lime + 5g contaminated soil	12.4	0	4000	0	22	82
0.1M HNO_3	5g Contaminated soil	1.2	858	2600	280	5	22.1
	0.1g Lime + 5g contaminated soil	1.2	711	51000	320	37	102
0.01M HNO_3	5g Contaminated soil	2.2	744	2400	270	4	19.6
	0.1 g Lime + 5g contaminated soil	11.9	3.2	22000	0	4	20

However, [Yukselen and Alpaslan 2001] have concluded the degree of heavy metal leaching is highly dependent on pH. Which is in agreement with the results of this study at using 0.1 M HNO_3,as leaching fluid highest release of lead was achieved. Al-Tabbaa et al [2005] reported that precipitation of salts in the high pH environment binding in contaminants occurs due to the pozzolanic reactions. In addition, Dermont et al [2008] mentioned the removal efficiency of different mineral acid types strongly depends on the metal type, the soil geochemistry and the reagent concentrations.

4.2.5 The effect of lime on metal contaminated soil

.The effect of adding lime to metal contaminated soil, includes: Pb, Zn, Ni, Cd ,Cr, Cu, the consequences of release of Cl^-, NO_3^- and SO_4^{2-} were also measured(see Table 4.10).

The effect were almost 99 % reduction of concentration of metals the final leaching solution, the pH were increase to 11.99. There was greater release of a nitrate about 9532.2µg/g, while in untreated soils it was 11707 µg/g, the sulphates were around 35 µg/g in untreated soils it was 28 µg/g and chlorine was 9.3 µg/g. While in untreated soils it was15 µg/g. in soils treated by 0.1 g of lime in the final solution there was not any detection by ICP AES for Zn, Ni, Cd, and Cu, while Pb and Cr were 7.2 and 2.5 µg/g respectively, where the standard deviation were higher in the measurement of lead (± 5.1) and in measuring Cr (±1.2). (see Table 4.10).

The maximum extraction was achieved by using acid extraction test for 1 g of metal contaminated soils, (see Fig. 3.4 in chapter 3).

According to Masahiro and Wada [2007] a certain amount of lime 50 g/ kg of calcite or slacked lime is effective in reducing the lead in the final solution. They also described that the soil is adsorbing the lead, and surface of soil materials are the negatively charged sites in layer silicate minerals and the surface functional groups including Si–OH, Al–OH, Fe–OH and COOH groups.

The desorption of Pb by acid can be expressed as:

$PbX^2 + 2H^+ = 2HX + Pb^{2+}$ (1)and $(SO)^2Pb + 2H^+ = 2SOH + Pb^{2+}$ (2)

where X stands for the negatively charged site in layer silicate minerals and SOH represents the surface functional groups

Lime is used widely in industrial processes and for geotechnical stabilisation of soils. Lime is discussed in detail below, because it illustrates the complex reactions that take place on the addition of a relatively simple material to pozzolans and soils. The interactions of cement and lime on soils are broadly similar, despite cement having a lower free lime content [Bone et al 2004].

Table 4.10 Effect of lime on release of a mixture of metals from contaminated soil(Pb, Zn, Ni, Cd, Cr, and Cu) leached with 50 ml of deionised water .

Sample	Pb (µg/g)	Zn (µg/g)	Ni (µg/g)	Cd (µg/g)	Cr (µg/g)	Cu (µg/g)	pH	Cl^- (µg/g)	NO_3^- (µg/g)	SO_4^{2-} (µg/g)
Metal contaminated soil + 50 ml DI water	857	880	905	987	881	927	4.1	17.1	0.03	20.7
Metal contaminated soil + 50 ml DI water	883	1065	1084	1193	902	1107	4.0	17	18751	33.7
Metal contaminated soil + 50 ml DI water	912	946	975	1056	933	980	3.9	11.2	16370	30
Mean	884	964	988	1079	905	1005	3.9	15.1	11707	28.1
Sd	27.6	93.71	90.2	104.9	26.15	92.54	0.09			
Metal contaminated soil + 50 ml DI water +0.1g lime	10.1	N/D	N/D	N/D	3	N/D	11.9	8.9	10673	28.46
Metal contaminated soil + 50 ml DI water +0.1g lime	0.007	N/D	N/D	N/D	1.1	N/D	11.9	9.8	7848.3	22.56
Metal contaminated soil + 50 ml of DI water +0.1g lime	11	N/D	N/D	N/D	3.52	N/D	12.0	9.9	10075	55/46
Mean	7.21				2.5		11.9	9.33	9532.2	35.49
Sd	5.19				1.2		0.12	0.55	1488.6	17..541

4.3 Characterisation of Precipitated Materials

Further investigation was required to explain the chemical reactions which occurred as results of conducting the leaching test and contact between the stabilized materials and contaminant either in solution or the soils. The most used chemical analytical tools were implemented in this field are Fourier transform infrared (FTIR), Raman spectroscopy, X-ray diffraction (XRD), and X-ray photo spectroscopy (XPS).

4.3.1 Fourier Transformation Infrared Spectroscopy

The FTIR method is described in (Chapter two, section 2.2.10). The materials were exposed for infrared analysis and the peaks were compared against untreated samples. When comparing the spectra obtained for contaminated soil and stabilised soil the FTIR spectra shows additional peaks. In each case the peaks due to the stabiliser material are different from the remainder. For instance, the spectrum of OPC with lead contaminated soil is different from the spectra of lead contaminated soil with lime. The difference in the curves can be ascribed to absorption that occurred in the surface of the contaminated soil with the stabiliser material, i.e lime in stabilized lead solution (Fig 4.3), there are different trough or peaks in Figure 4.3 which highlighted the different, the drops and peaks were recorded as a shifting in different transmission numbers, the two peaks at 970cm^{-1} and 670cm^{-1} were attributed to Si-O, Si-O-H and at 1570 cm^{-1} attributed to O-H.

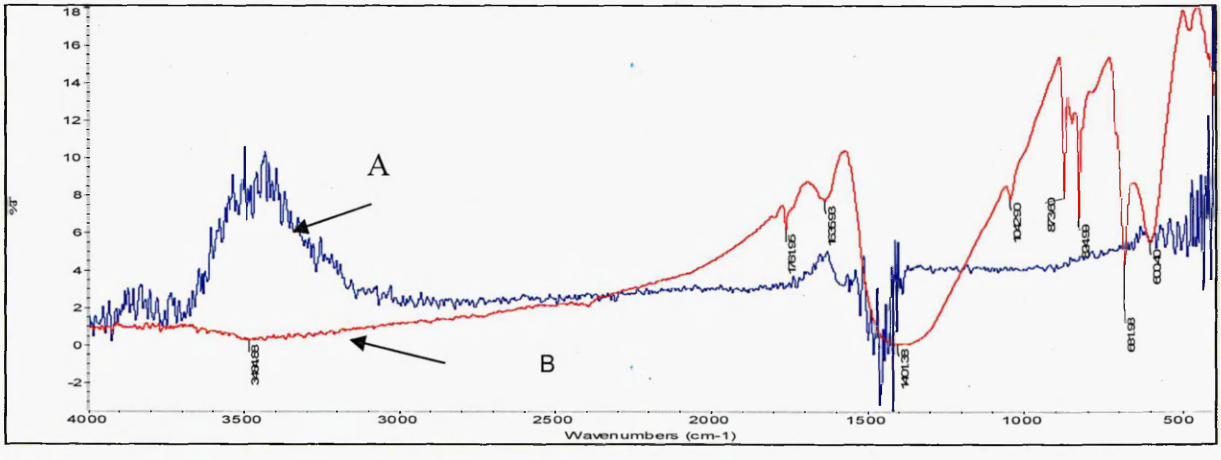

Figure 4.3 FTIR spectra of Lime and Pb solution treated with Lime, (A)- Lime spectra line, (B)- Lime treated Pb solution

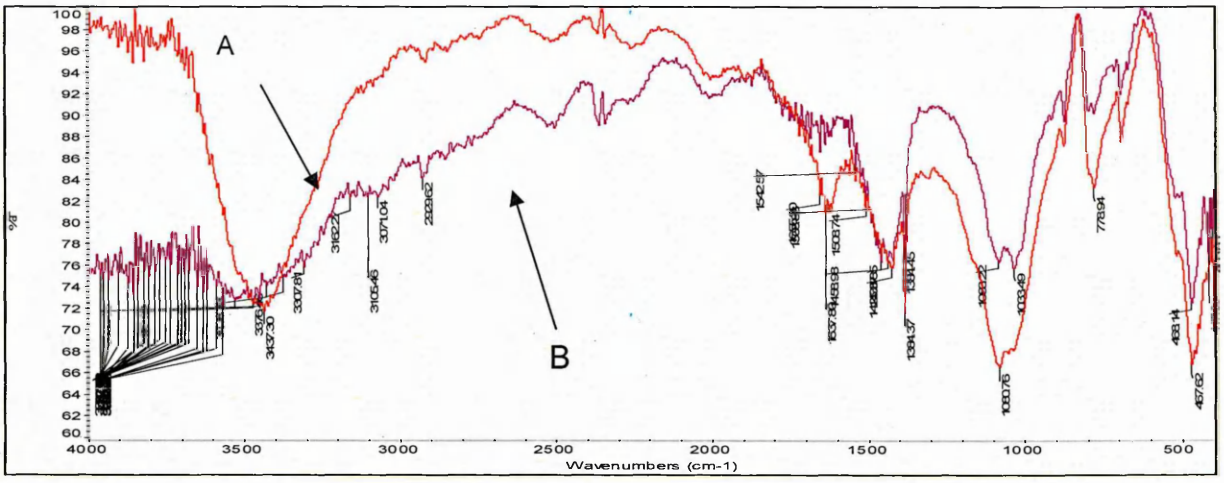

Figure 4.4 FTIR Spectra for (A)- lead contaminated soil spectra and (B)- lead contaminated soil treated with lime

In lime stabilised lead contaminated soil it is obvious to see different peaks representing the lime at 900 cm^{-1} which referees to Ca bond also a drop at 1200 cm^{-1} which referees to Carbonate that can be read as $PbCO_3$. Table 4.11 summarise the peaks found by comparison between the lime as references peaks and both contaminated lime and lime treated lead contaminated soil along with previous work done by Barnnett et al [2002] identify the FTIR spectra, in addition to soil vibration frequencies according to López-Lara [2004] the peaks 1083, 1033 cm^{-1} in spectra of treated soil are assigned to $V3.SO^{2-}_4$. According to Barnett et al [2002], Table 4.11 can be referred to the present of lead in the specimen as $PbSO_4^{2-}$, since it is the lead which is precipitated on the surface, also peaks at spectra of treat soils with peaks 3105, 3160, 3307 cm^{-1} is assigned to symmetric and asymmetric stretching (Vl andV3 of O-H) that might refer to PbOH compound,. There are not clear peaks to refer to presence of Ca in the samples since the peaks at 3530 cm^{-1} afar from 3645 cm^{-1} which is assigned to stretching O-H of $Ca(OH)_2$.

Table 4.11 Principal FTIR frequency bands in hydrate Portland cement according [Barnett et al 2002] and compared with data obtained in this study

Wave number (cm-1)	Assignment	lime treated soil in this study	Lime +Pb solution in this study	Lime in this study
3645	stretching O-H of $Ca(OH)_2$	3530		
3100-3400	symmetric and asymmetric stretching (Vl and V3 of O-H	3105, 3160,3307	3484	3380
1650	Deformation(V2)H_O_H	1642	1636	
1480	$V3.CO_3^{2-}$	1459	1401	1478
872	$V2.CO_3^{2-}$		873	
712	$V4.CO_3^{2-}$		682	
970	stretching Si-O(V3) (in polymeric unit of SiO_4^{4-})			
925	stretching Si-O(V3) (in non-hydrated cement)			
522	V4.Si-O		500	521
452	V2.Si-O	468	457	452
1115	$V3.SO_4^{2-}$	1083, 1033	1042	

4.3.2 Raman Spectroscopic Analysis

Raman spectroscopy is sensitive to the presence of calcium carbonate; it thus offers a ready assessment of the extent of its presence in the samples and is a useful technique for finger-printing of the material. This is seen by comparing the two curves at uncontaminated soil spectra with lead contaminated soil spectra or lead contaminated soils and lime treated soils or lead contaminated solution and treated lead solution spectra, the procedure of conducting the measurement are described chapter two.

In Figure 4.5 the peak at 1045 cm^{-1} show the presence of lead in the contaminated soils, spectra in B line, peak at 1045 cm^{-1} belongs to lead contaminated soils, since it is not present in blank soils. The soils were contaminated with 20,000 mg/l of lead solution in order to enable the Raman instrumental to detect the lead in the samples, as it has a relatively high detection limit.

In figure 4.6, lime treated lead contaminated soil, not many peaks were observed by Raman, this may be attributed to curing effects, that it was not physical binding between the contaminated soils and the lime stabilizer. The only peak is at 455 cm^{-1} which was, present also in contaminated soils, there is only a small peak under close to 200 cm^{-1} which it might

be attributed to Ca-O vibration, according to Kirk.et al [1997] that would suggest presence of Pb-CaO.

In Figure 4.7, for 0.1g lime in 50 ml of deionised water, the other with 0.1 g of lime added to lead solution. This is seen by comparing the two curves in Figure 4.7 , the one for lime in a solution of de-ionised water The lead solution was 20 000 mg/l to enable the Raman to detect the lead in the samples (see figure 4.7).

The main peaks in stabilized solutions (see Fig.4.7) are 390, 701, 1045 cm^{-1}, which is According to [Kirkpatrick. and Yarger, 1997] (see Table 4.12), is assigned to Ca-O, symmetrical stretching of silicate tetrahedral carbonate group) and silicate groups. Those peaks are referred to lead formation in treated samples, which can be referred to Pb-Ca-O or $Pb\text{-}SO_3$, $Pb\text{-}Ca\text{-}SO_4$ which are the same compounds confirmed by other techniques (FTIR see section 4.3.1, and also by XRD, section 4.3.3). Figure 4.7 shows very similar peaks, except at 1000-1050cm^{-1}, where the contaminated soil sample shows a strong peak, which is due to the lead silicate carbonate group [Kirkpatrick and Yarger, 1997] also according to Gibbs et al [2010] it is $2PbCO_3.Pb(OH)_2$. The lead had reacted with the silica and carbonate present in the soil. The v_1 and v_4 vibrations of the carbonate were observed at 1084cm^{-1} and 712cm^{-1} respectively, and the lattice vibration at 280cm^{-1} is due to Ca-O.

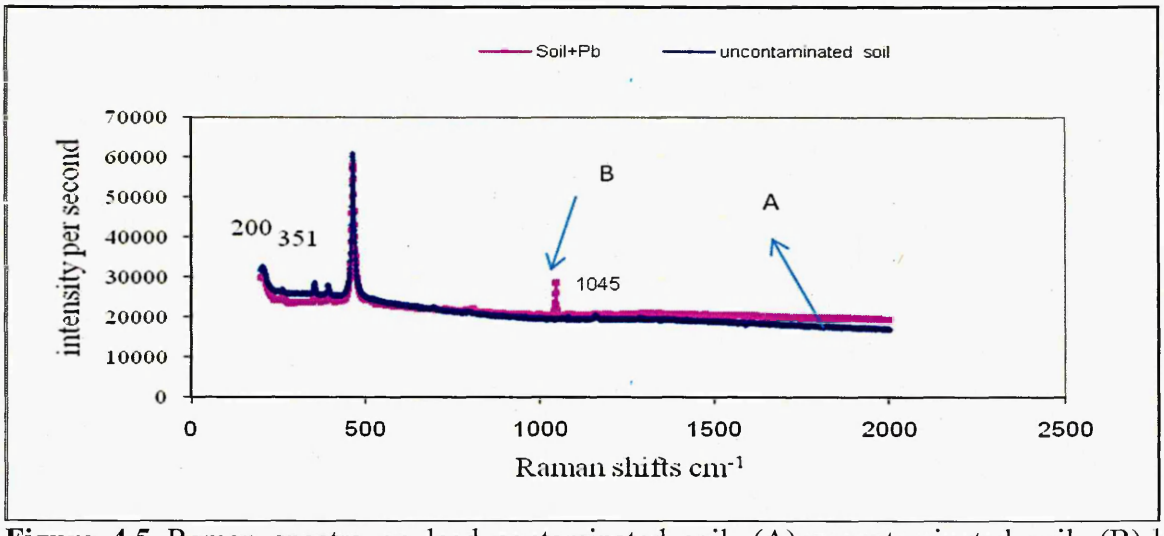

Figure 4.5 Raman spectra on lead contaminated soil, (A)-uncontaminated soil, (B)-lead contaminated soil

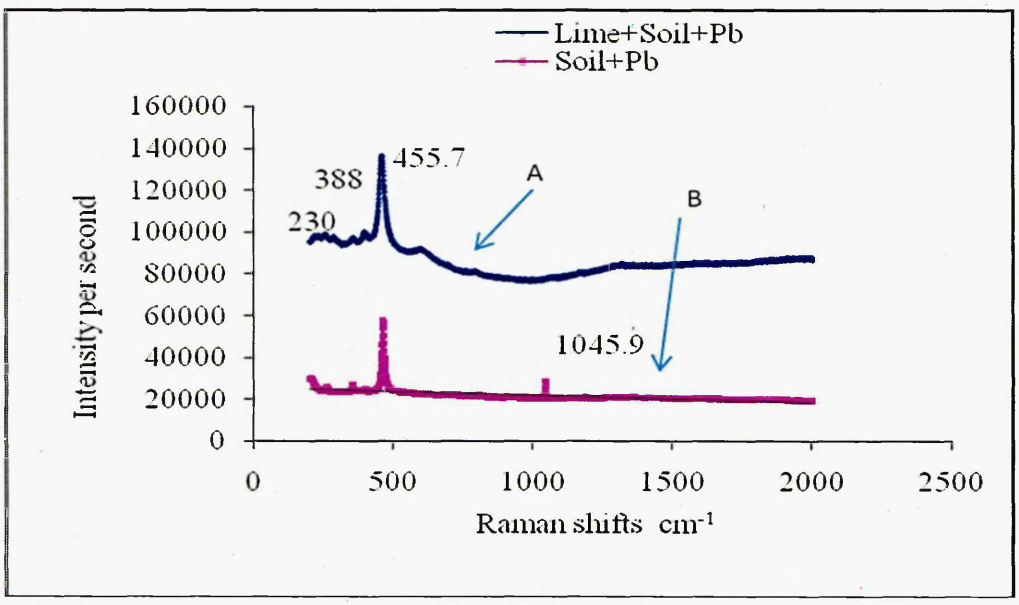

Figure 4.6 Raman spectra on lead contaminated soil and Lime treated soil, **(A)** .Lime treated contaminated soils, **(B)**.lead contaminated soils

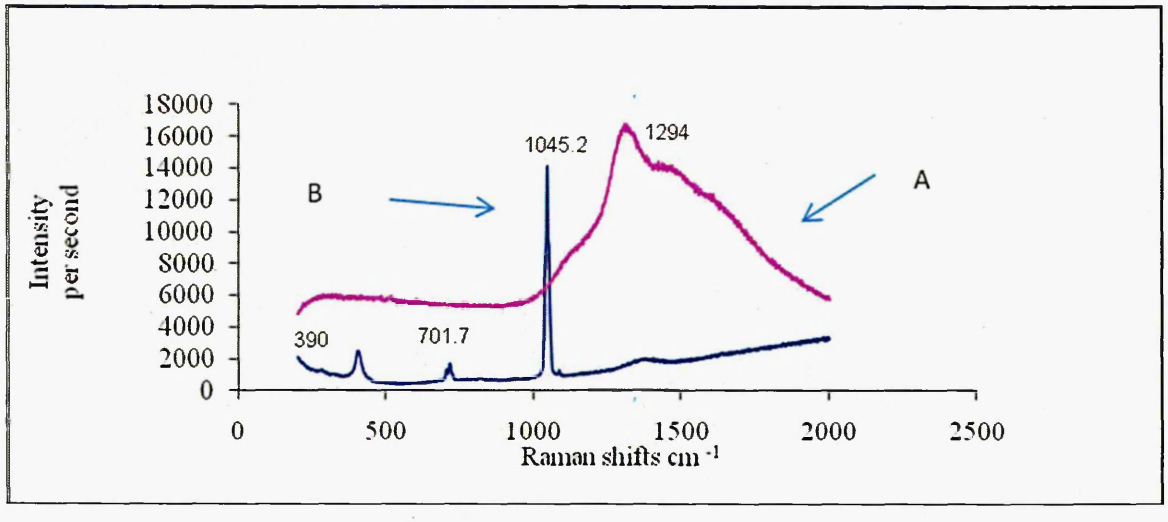

Figure 4.7 Raman spectra on Lime stabilized lead solution, (A)- blank lime ,1g of lime in 50ml of deionised water (B)- 0.1g of lime stabilized Pb solution

Table 4.12 Raman frequencies of the principle band in hydrate Portland cement [after KirkPatrick 1997] compared with results in this study

Band Cm^{-1}	Origin	Lead contaminated soil treated with lime in this study	Lime stabilized Pb solution in this study
200-400	Ca-O vibration	351	390
430-540	Internal deformations of Si-O, tetrahedra (O-si-Obending)	455.7	
600-700	silicate Group		701.7
800-1100	symmetrical stretching of silicate tetrahedral carbonate group) Symmetrical stretching (SS) of Si-O tetrahedral.	1045.9	1045
3000-4000	OH vibration		

4.3.3 X-ray Diffraction (XRD) Investigation

The XRD examined the soil contaminated with lead and treated with lime, in comparison with the soil sample containing lime but no contaminant lead. The results of the analysis suggests that $PbCO_3$ or $Pb(OH)_2$ may have formed on the surface. This is not unlikely as the main constituent of lime, over 60%, is Ca in the form of CaO, $CaCO_3$, $CaC(OH)_2$.

Adding lime to lead solution with a scan from 5 - 80 theta for 2 hours and for lime with no added lead, many peaks were seen, as in Fig.4.8, however according to international database (www.cds.dl.ac.uk) to identify those peaks, the formation compounds were as follows, Pb_2CO_3, Pb_2OCO_3, $Pb_2Al(SO_3)$, Pb SO_3,$PbSO_4$. (See Fig. 4.8 and 4.9). In lime stabilized lead contaminated soil, spectra no peaks, can be identified by XRD indicating no formation of any compounds which can be referred, due to no physical binding between the contaminated soil and lime.

The results show that the curing time plays a role in the reaction set up,in this study it was not any physical binding between the contaminated soil and lime additives , which known as mould or physical binding . In addition, FTIR spectra see section.4.3.1 is in correlation with those finding by XRD, also XPS and ESEM support this results(See Section 4.3.4 and 4.3.5).

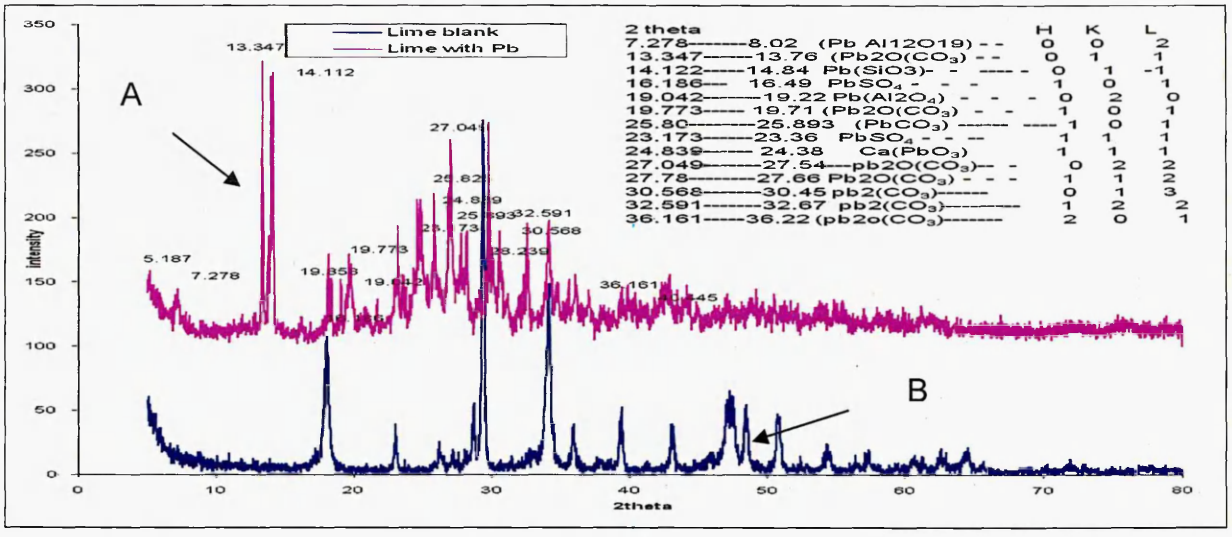

Figure 4.8 XRD Spectra for lime stabilized Lead solution.(A)lLime stablized Pb soltuion,(B) lime with no lead solution.

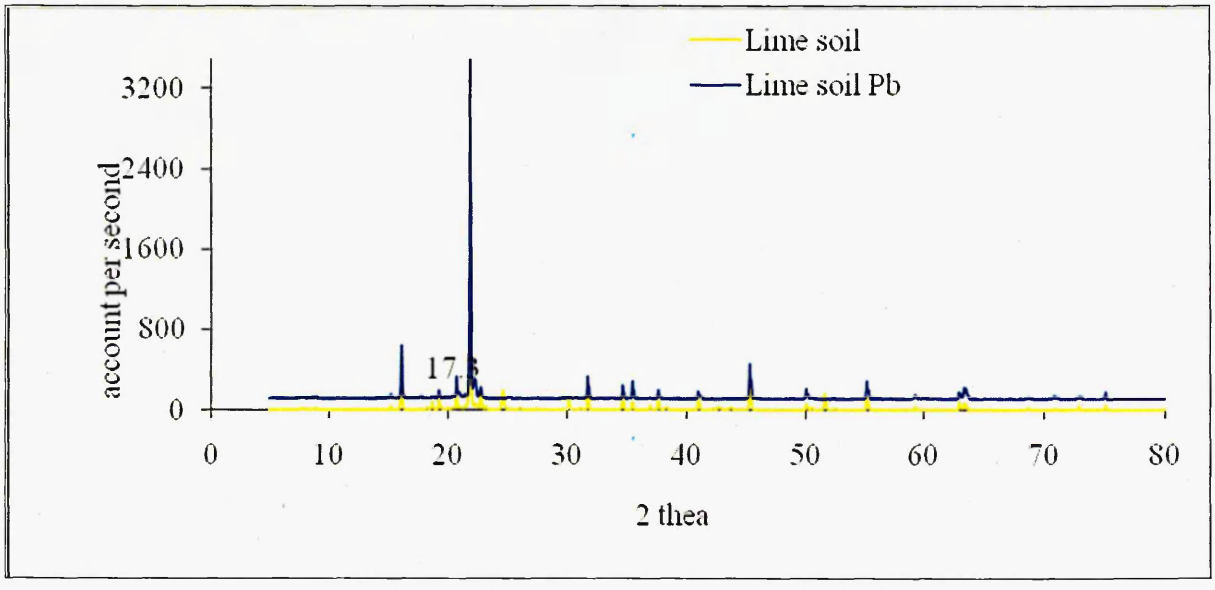

Figure 4.9 XRD spectra for 0.1 g of Lime stabilized lead contaminated soil, contamination solution strength 20,000mg/l

4.3.4 Environmental Scanning Electron Microscope

ESEM provides more evidence of the binding of Pb particles on the surface of lime, which prove the mobilization and participation of Pb. These techniques are used for qualitative analysis not for quantitative. On the surface of lime particles, an EDAX energy dispersive, spectroscopy (EDS) detector. Typically, a spot size of 3 μm and a 20 keV electron beam were applied, the work distance was varied unlit get the correct image of identity the lead particle

in the sample, the EDX shows qualitative amount of calcium and lead in specimen where ESEM image identified the spectra or the spot of element in the image. In addition EDX analysis the elements associated at the spot of image are Ca, O, C (see Fig.4.10a and Fig.4.10.b).

In addition, the ESEM for lime treated soils proved the presence of lead in the treated soil (see Figure.4.11a and EDX 4.11.b).The mapping for analysis of the elements were considered, Al, K, Mg, Pb and O. Taube et al[2008] have used similar techniques to ESEM to analyse the morphology and compositions of soil contaminated with mercury. In this study lead was found to be concentrated in spherical bright particles (see fig. 4.10a and 4.11a)which in agreement with Taube et al[2008].

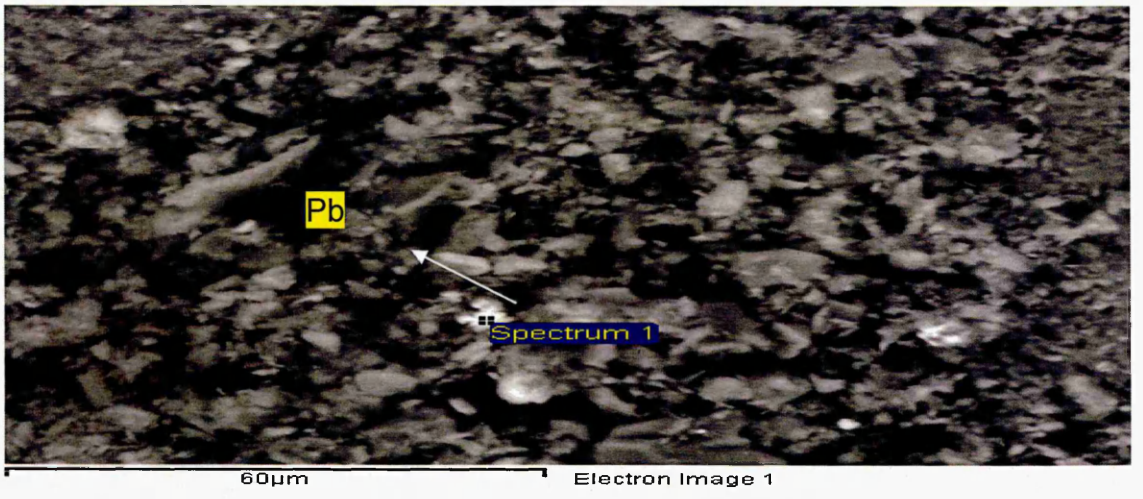

Fig 4.10 a ESEM image for lime treated lead contaminated soils. Spectra 1 represents lead

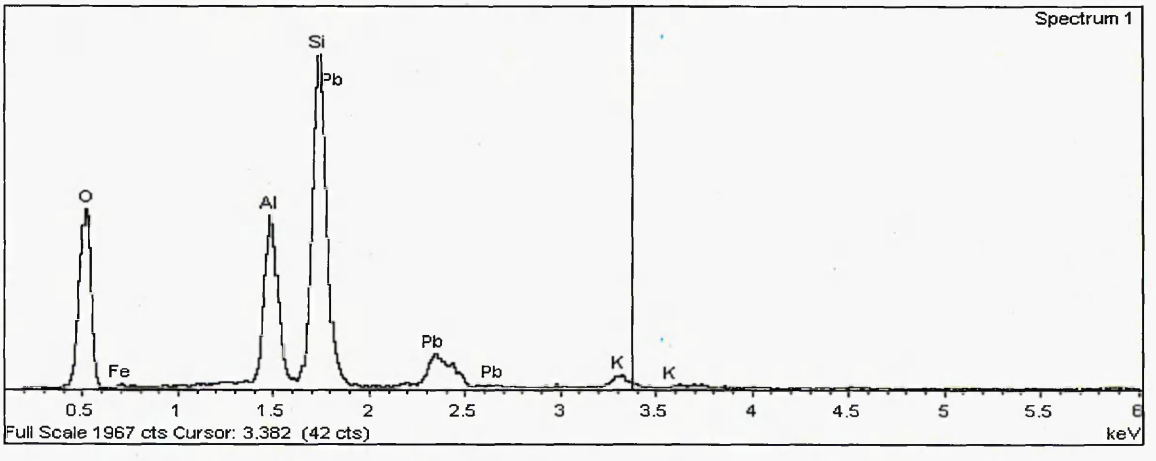

Fig 4.10.b EDX analysis for ESEM image 1 for lime treated lead contaminated soils, spectra1 for Pb and associated elements (Al, Pb, Fe, K, Si, and O)

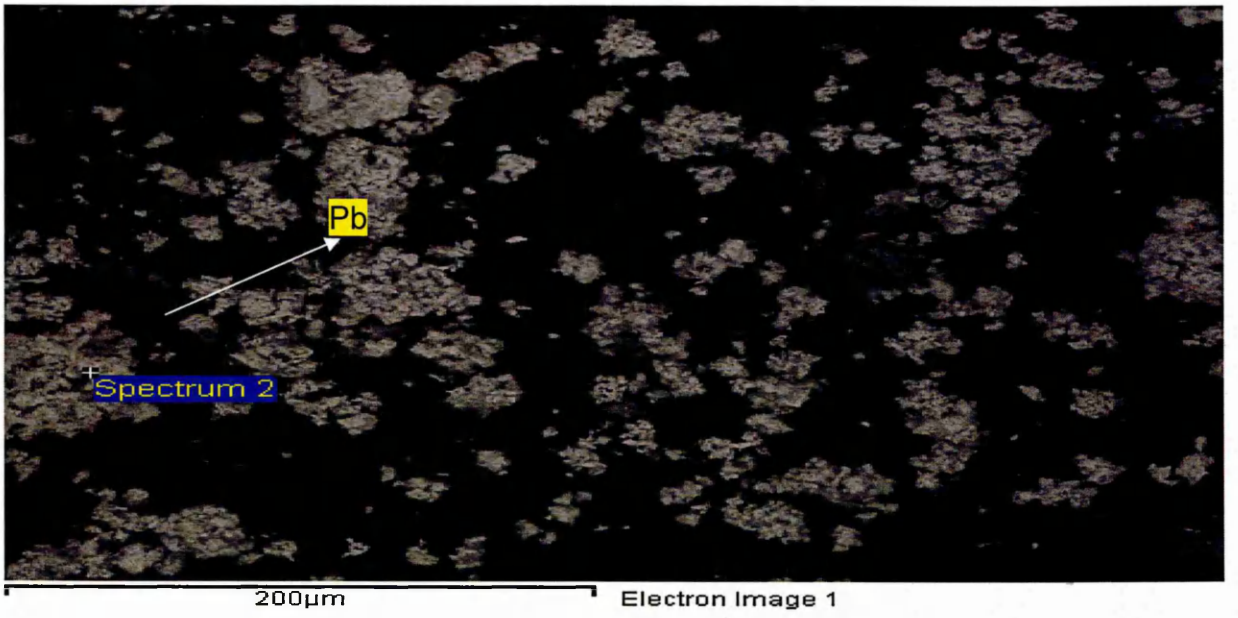

Figure 4.11a ESEM image 0.1 g of Lime stabilized 1000 Pb solution, spectrum2, Pb 200µm E.M work distance, spectra 1 Pb

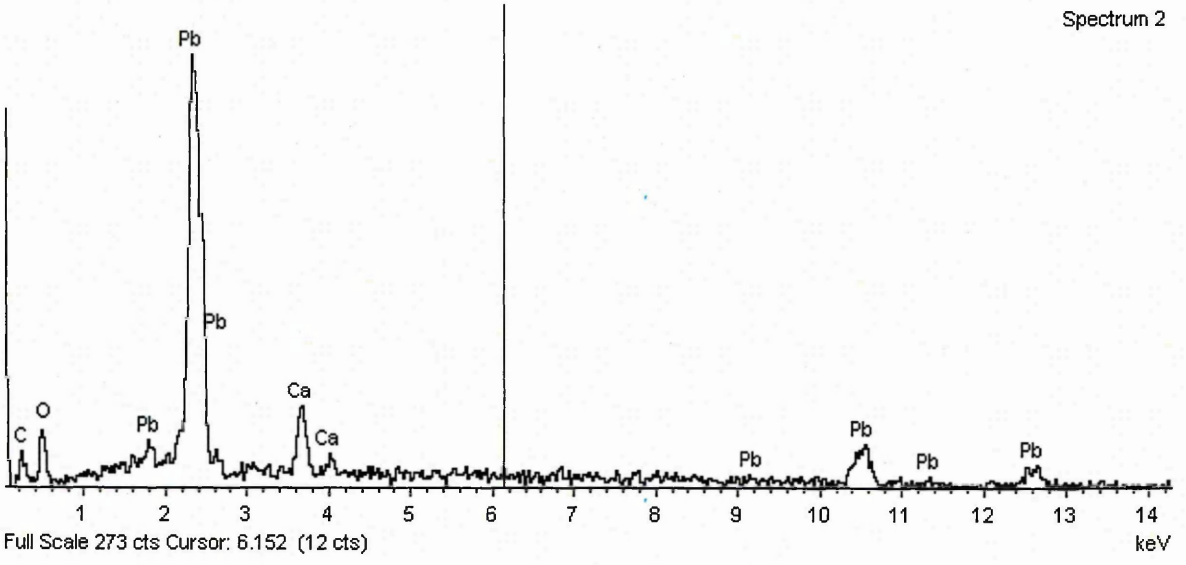

Figure 4.11b EDX analysis spectrum 2 for ESME image on lime stabilized Pb solution, spectra1Pb associated elements (Pb, Ca , C and O)

4.3.5 XPS investigations

X-ray photoelectron spectroscopy (XPS) studies were performed to complement the EDAX (energy dispersive X-ray) analysis. Whereas EDAX provides a bulk atomic composition, XPS is a surface analytical technique sensitive to the first 100 Å of the solid surface. XPS is also capable of identifying oxidation states. Particle concrete samples were mounted for the analysis by pressing the powder into conductive carbon adhesive pads attached to the standard 1 cm diameter stainless steel sample stubs.

4.3.5.1 XPS investigation for lead contaminated solution

The XPS provides extra powerful information on characterisation the samples of lime treated lead solution. In Fig.4.12 a wide scan of XPS spectra on blank lime with deionised water shows no lead peaks in the spectra and demonstrates the elements that make the lime which are Ca, K, O in comparison with a wide scan of XPS for lime stabilised lead solution (see Fig.4.13). In this spectra the Pb4f were clearly presented in the specimen and positioned at 138 eV, which is only attributed to Pb 4f. In comparing with spectra of blank lime in Fig 4.12 the amount of Ca were higher due to none lead in blank lime. The explanation of low Ca2p in Fig 4.13, is the replacement of Pb ion to Ca ion which is attributed to ion exchange reaction between the Ca and Pb in presence of water. However, according to the XPS spectra standard database, which generally provide sufficient data for the determination of chemical states for uncomplicated (i.e. single peak) spectra, the main formation of lead compounds Pb4f are given to $PbCO_3$ and PbO, see Fig.4.14. However, according to James et al [2008]. The binding energy at 138 eV and the doublet 141 eV are assigned to PbO, or Pb SO_3 . The FTIR and XRD are in supporting of these results, see section 4.3.1 and 4.3.3 and also ESEM investigation see section 4.3.

In addition. Daeik et al [2009] observed that Pb $4f_{7/2}$ and $_{5/2}$ doublet were observed at 140 and 145 eV and insufficient to distinguish PbO from PbO_2 or $PbSO_3$, or even $PbSO_4$ and concluded that the survey scan is sufficient to distinguish metallic lead from the oxidized forms .

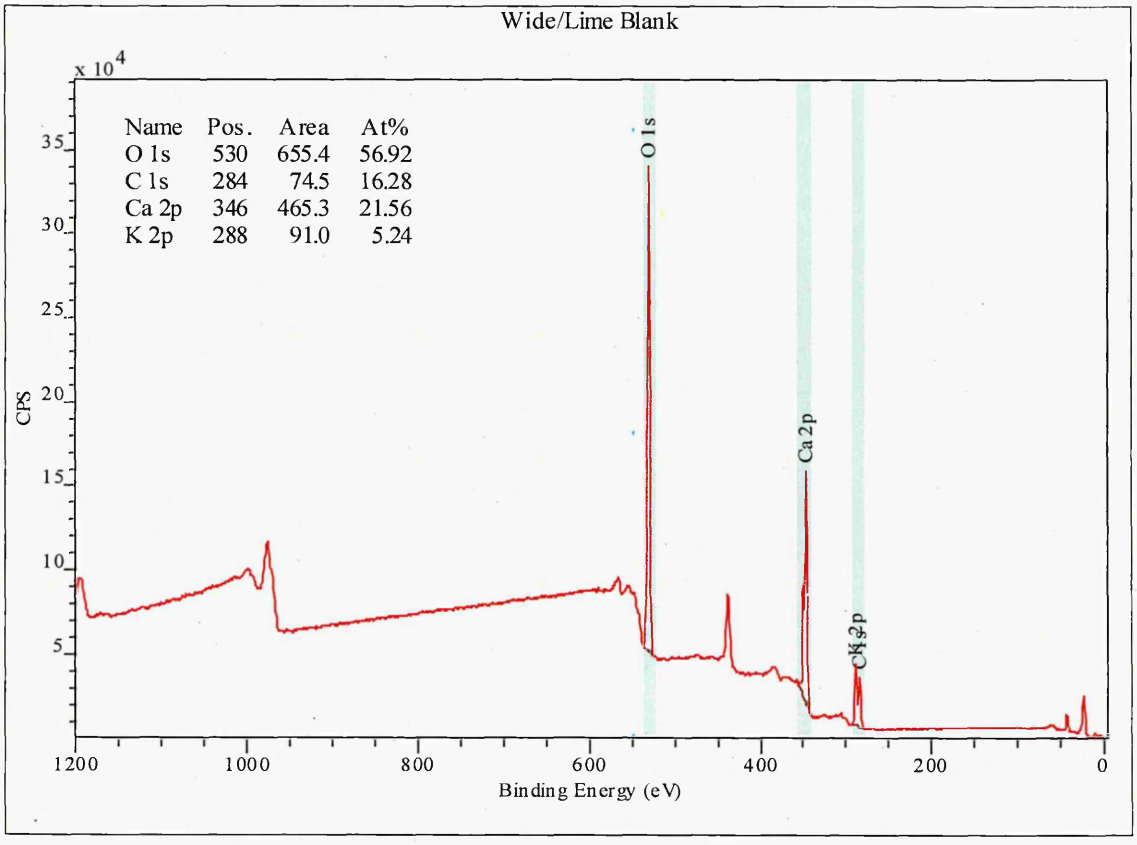

Figure 4.12 Wide scan of XPS spectra of lime blank (deionised water and lime)

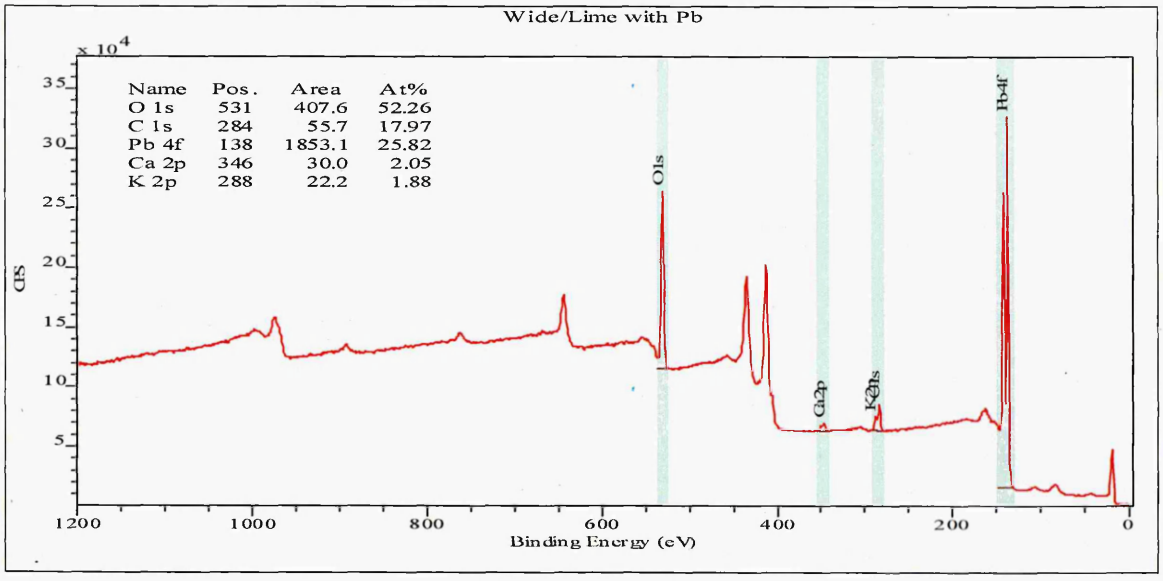

Figure 4.13 XPS wide scan spectra for 0.1 g of lime stabilized 50ml of 20,000 mg/lead solution

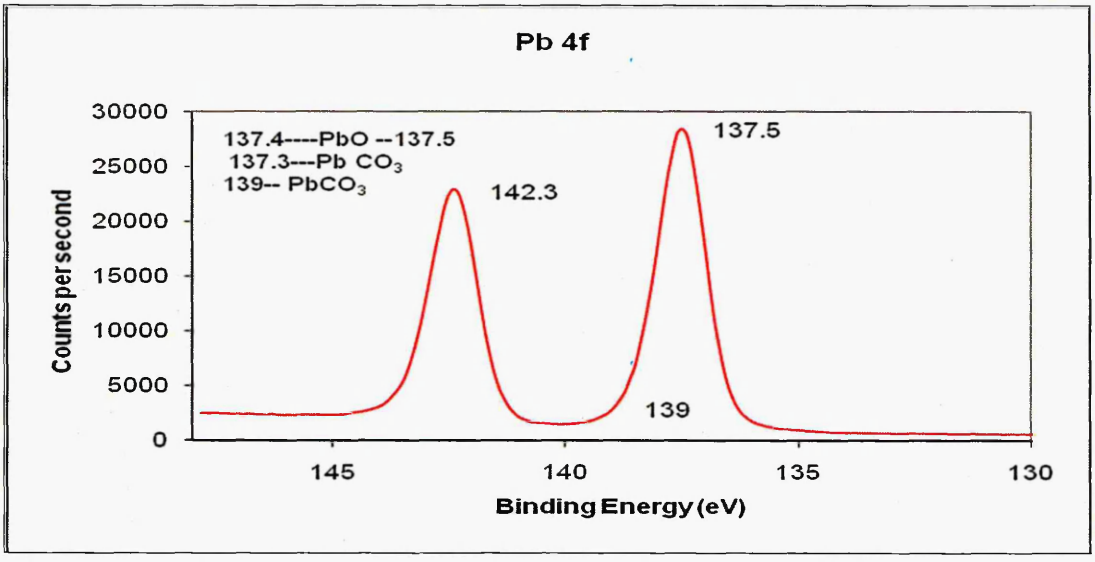

Figure 4.14 Detailed XPS analysis of the spectrum for lime treated lead contaminated solution, over the region of the lead 4f spectral line

4.3.5.2 XPS investigation of lead contaminated soils and treated soils

Figure 4.15 presents a wide scan of lead contaminated soil; it shows clearly the position of lead Pb4f at binding energy peak 136 eV, occupied about 0.91. The majority of elements were O 1 s, Si2p, and Na1s, which occupied 55, 20 and 4 %, respectively. While Ca2p only accounts for 1.18 %. (see Figure 4.16 and 4.17). However the peaks 136 eV are assigned to Pb4f7 according to XPS international data base, and 141 eV is assigned to Pb4f5. In classification to the chemical state for those peaks and relaying to James,.et al [2008] and [Tyczkowski and Pietrzyk.1998] the 137 eV and the doublet 141 eV are assigned to PbO, PbO_2 or $PbSO_3$.

Similarly Fig. 4.18 shows the wide scan of contaminated soil treated with 0.1g lime, compared with untreated sample (see Fig, 4.16).The Pb occupied 0.55 % reduced from 0.91% in untreated soil. Ca2p occupied 0.50% and Si to 23% from 20.14 % in untreated samples, the Pb 4f at doublet peaks 136.5 and 141.3 (see Fig.4.19), however in regard to James et al [2008] these peaks are assigned to $PbSO_3$ and $PbSO_4$. Also many other compounds of lead are present (see Fig. 4.19) which are in agreement with the results obtained by XRD and FTIR.(See section 4.31.4.3.2 and also 4.3.5). The multi-peaks in Fig.4.19 shows that many compounds were formed in the region of Pb4f, those compounds are for Pb at the region of BE from 138.2 eV to 144 eV, such as $Pb4f_{7/21}$ and $Pb4f_{5/21}$,$Pb4f_{7/22}$ and $Pb4f_{5/22}$.

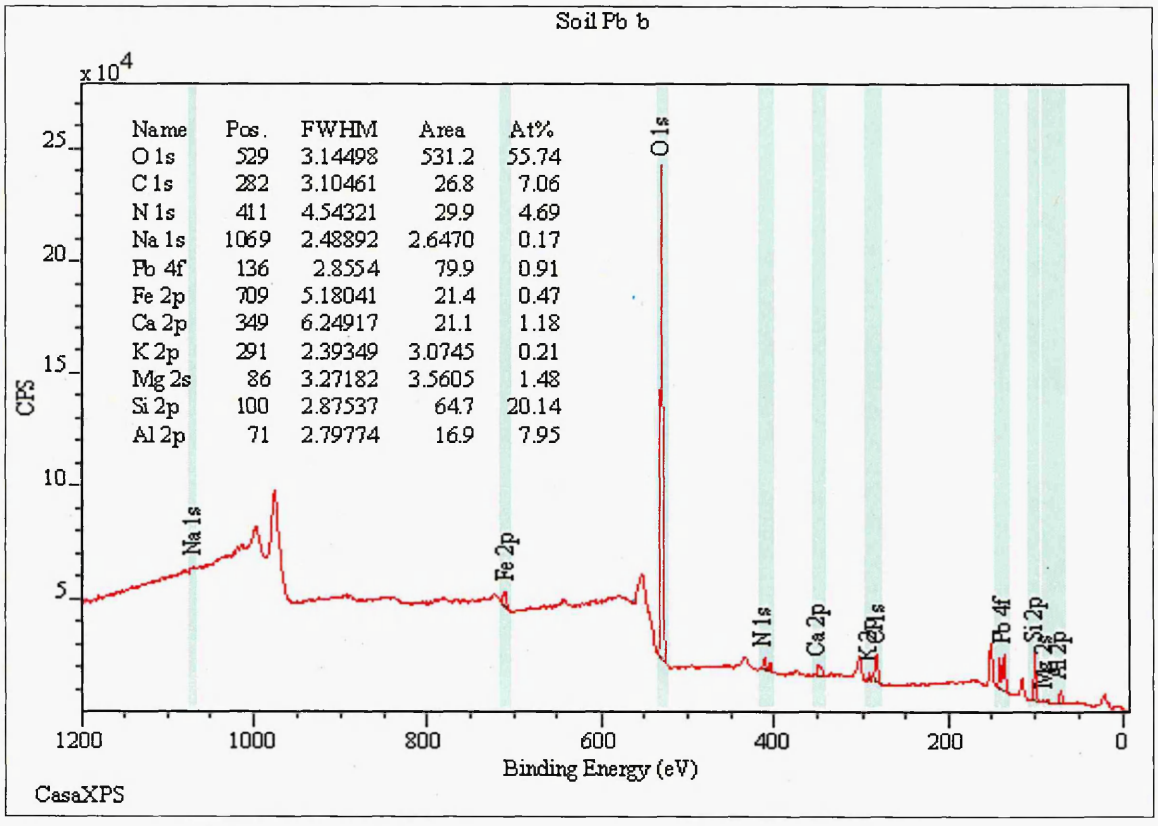

Figure 4.15 Wide scan of XPS spectra of lead contaminated soil

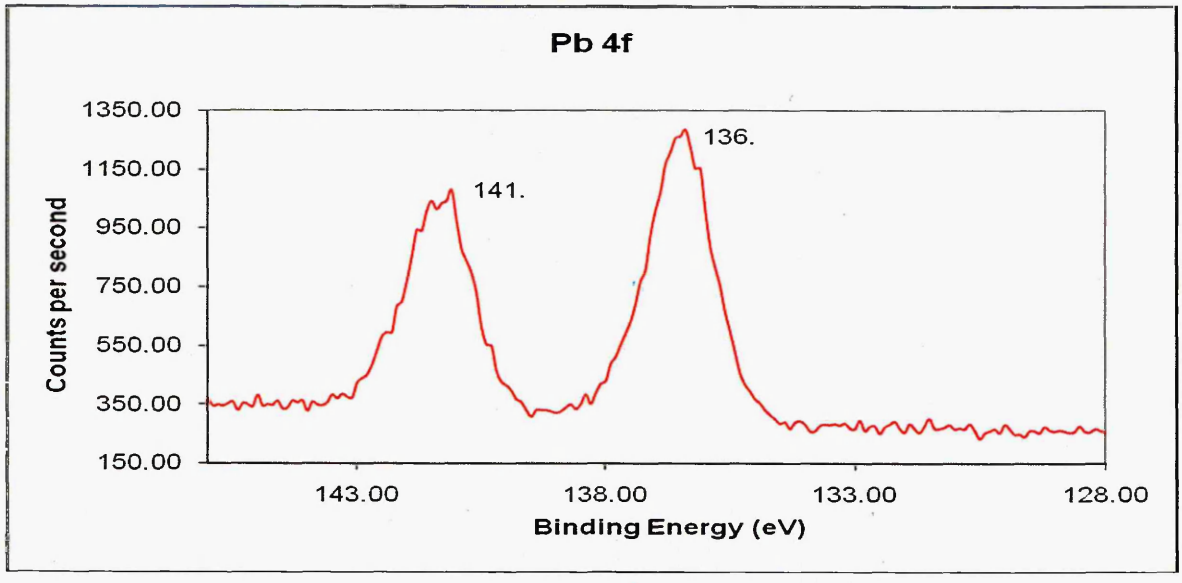

Figure 4.16 Detailed XPS analysis of the spectrum for lead contaminated soil, over the region of the lead 4f spectral line

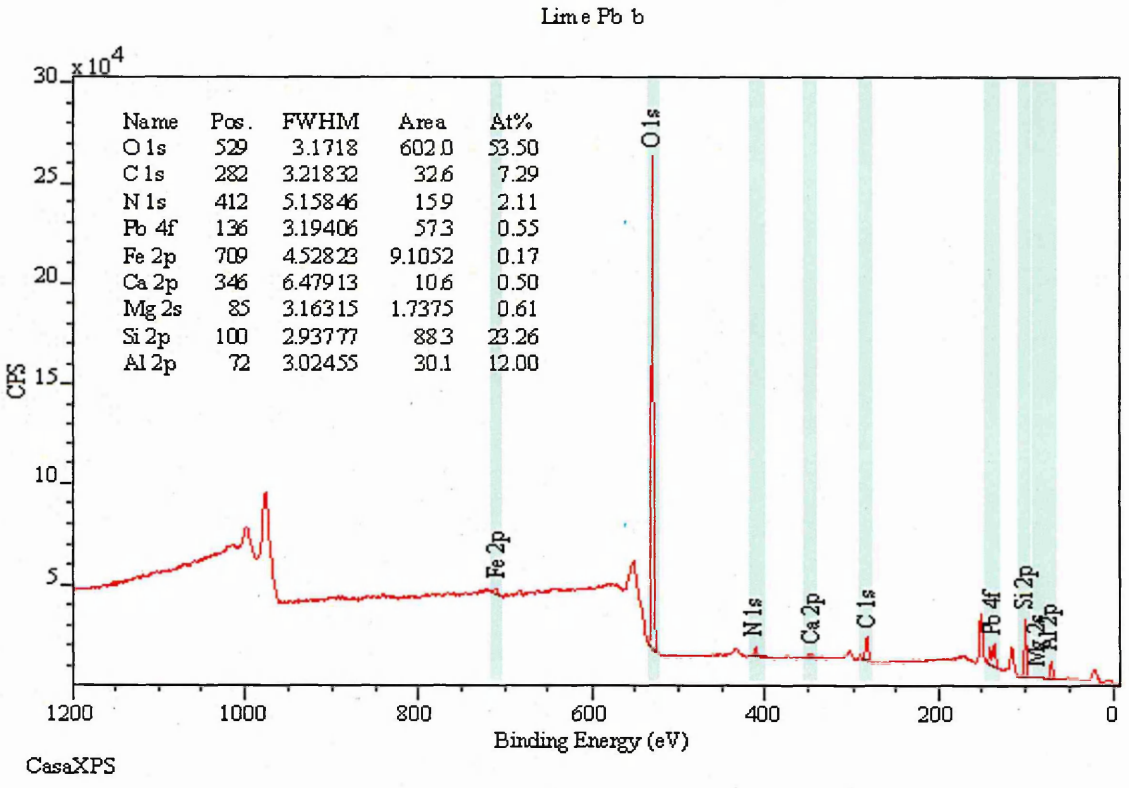

Figure 4.17 Wide scan of XPS spectra of 0.1 g of lime a stabilized 5 g of Pb contaminated soil, leached with 50 ml of deionised water

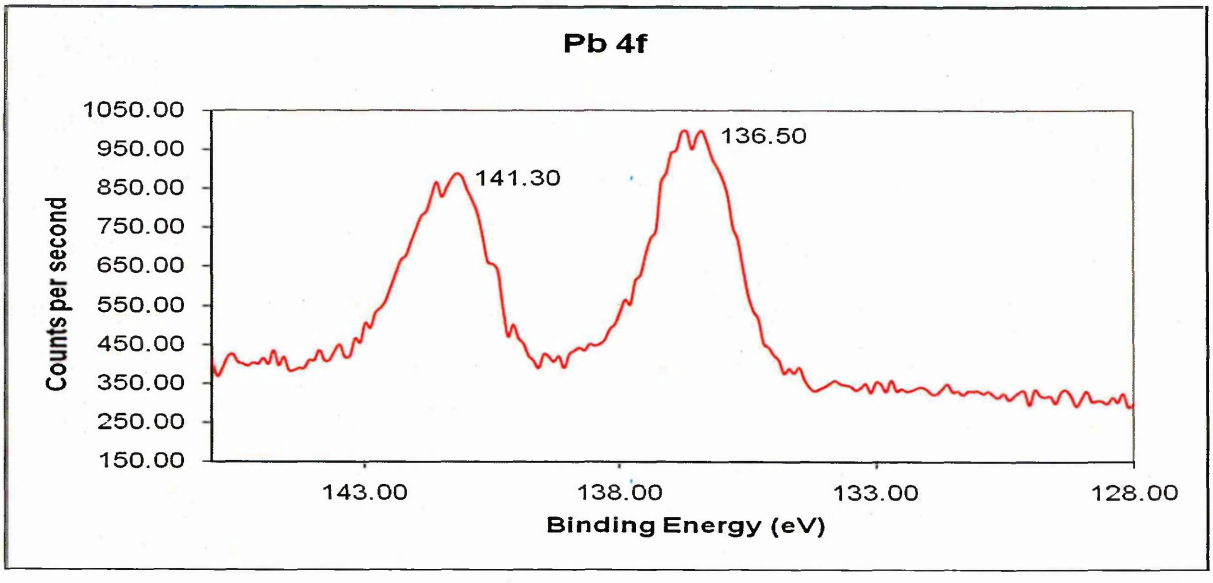

Figure 4.18 Detailed XPS analysis of the spectrum for lime treated lead contaminated soil, over the region of the lead 4f spectral line

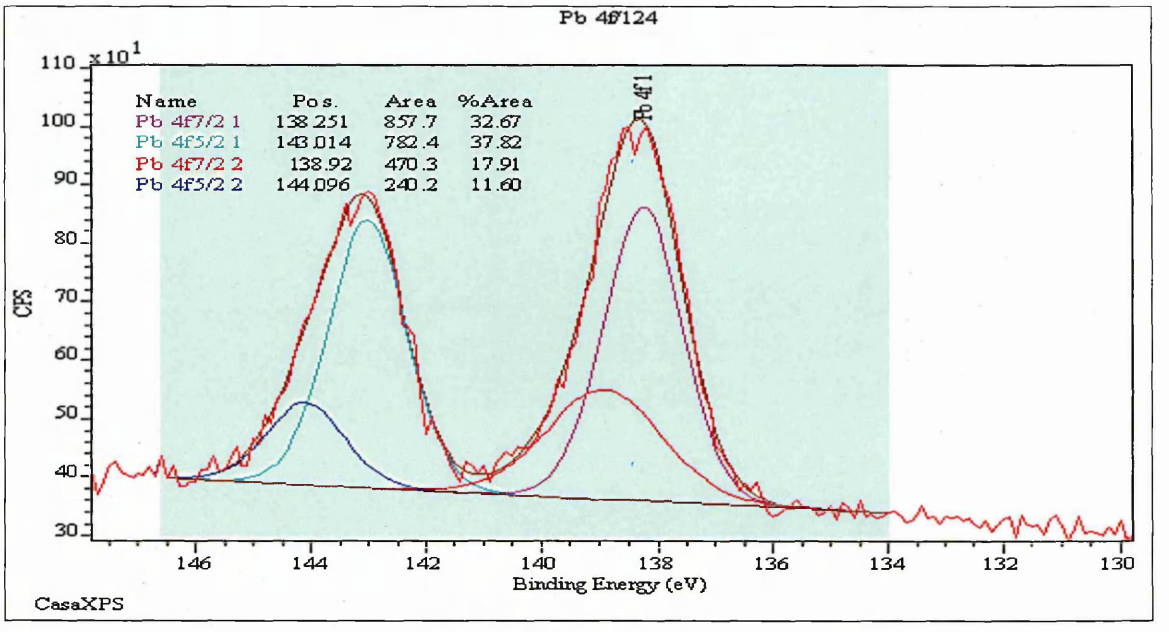

Figure 4.19 Detailed XPS analysis of the spectrum for lime treated lead contaminated soil, over the region of the lead 4f spectral line

Chapter Five

Effect of Magnesia on metal contaminated soils and solutions

5.1 Methods for measurement of the leachibility of lead

The soils and level of lead contamination used to investigate the effect of adding magnesia were the same as those used in previous chapters, as described in chapter 2 sections 2.2.4. Furthermore, the leachability of lead was determined in a manner similar to that described fin Section 2.2.5, and also in Chapters 3 and 4, see Table 3.1 where the maximum extraction was 780.8μg/g .

5.2 Compositions of magnesia and effect of magnesia of metal contaminated soils and solutions.

The composition of MgO powder and the uncontaminated soils was investigated using X-ray Fluorescence (XRF) as described in Chapter 2 and the results are shown in Table 5.1. The average pH of 5 uncontaminated soil samples in 50 ml DI water was 6.9 and 0.1 g of magnesia mixed in 50 ml deionised water resulted in a pH of 10.3, where the S/L ratio was 1:10.

Table 5.1 Chemical composition (by mass %) for magnesia and soil pH value of MgO and uncontaminated soil solutions (S/L ratio 1:10).

Compound (Mass %)	pH	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	Mn_3O_4	Fe_2O_3	ZnO	BaO
Magnesia	**10.3**	0.02	87.76	0.11	0.68	N/D	0.14	N/D	0.74	N/D	0.01	0.1	N/D	0.01
Uncontaminated soil	**6.9**	0.21	0.13	2.89	93.62	0.02	0.06	1.72	0.12	0.08	0.01	0.65	0.01	0.03

The composition of magnesia is different from that of the other materials such as OPC, lime, PFA, or GGBFS used in previous chapters to stabilize heavy metals. The different is in amount of CaO and MgO and Si, which is varied amount of content in each material See chapter, two Table 2.3 for the characterization for each material.

The investigation also measured the pH of 5 lead contaminated soil samples in 50ml of deionised water, and 5g of lead contaminated soil in 50ml of deionised water with 0.1g of MgO added, the average value was 10.3 The procedures for introducing the contaminant to the soil are explained in Chapter 2 (section 2.2.2).

5.2.1 The Effect of magnesia on lead contaminated soil

The effects of magnesia on contaminated soil were measured using the same method as for OPC described in Chapter 3. 0.1g of magnesia powder was mixed with 5g of contaminated soil in a polypropylene bottle, and 50ml of deionised water was added as the leaching fluid. This then shaken for two hours on a platform shaker at a rotary speed of 300 rpm. The filtration of the final solution and the measurements by ICP (AES) were similar in Chapter 3. The results are presented in terms of mass, μg/g, see Tables 5.2.and 5.3, 5.4. However, 0.1g of magnesia is equivalent to 2% of the total solid weight of the soil. The difference in pH levels shown in Tables 5.2 and 5.3 (pH = 5.5 and 4.6, respectively) for the final leaching solution with contaminated soil is due to more lead being present in the sample. The lead extracted (42.5μg/g) was higher in the latter case, which indicates a lower pH, see Table 5.3. Also the lead extraction obtained was higher when the contaminating solution for preparing the contaminated soils was of higher strength (20,000 mg/l), although magnesia was still effective as a stabiliser (Tables 5.2, 5.3 and 5.3).

Table 5.2 Effect of 0.1g magnesia on lead contaminated soil and subsequent release of Mg, Ca, Na, K and change in pH with addition of Magnesia. The strength of the contamination solution 1000 mg/l and speed 150rpm.Concentration in final leaching solution(n=3)

Sample	Pb (μg/g)	Mg (μg/g)	Ca (μg/g)	Na (μg/g)	K (μg/g)	pH
5g Lead contaminated soil + 50ml DI water	24.9	13.9	87.8	2.7	11.2	5.2
5g Lead contaminated soil + 50 ml DI water	32.1	17.1	120	4.2	12.4	5.8
5g Lead contaminated soil + 50 ml DI water	21.4	14.2	108	3.4	11.8	5.5
Mean	26.1	15.1	105	3.4	11.8	5.5
Sd	0.54	1.76	16.2	0.75	0.6	0.26
5g Lead contaminated soil + 0.1g MgO + 50 ml DI water	0.89	399	210	4.8	9.9	10.6
5g Lead contaminated soil + 0.1g MgO + 50 ml DI water	0.71	375	216	5.2	10.6	10.6
5g Lead contaminated soil + 0.1g MgO + 50 ml Di water	0.67	381	213	4.9	10.2	10.7
Mean	0.76	385	213	4.96	10.2	10.6
Sd	0.01	2.90	2.90	0.20	0.35	0.08

Table 5.2 shows a substantial increase in pH level from 5.5 to 10.6, when the contaminated soil was treated with magnesia. [Wada and Ono, 2006; Rotting et al 2006] also reported that using magnesia changed the pH to between 7 and 10.6. They also reported a large release of Mg, attributed to the Mg content of the magnesia, see Table 5.1. As a result of the increase in pH to 10.6, the Pb was mobilized and reduced to below 1mg/l in the final leachant. Which means there was a reduction of Pb in soil of about 95%, see Tables 5.3 and 5.4. Garcia et al [2004] achieved an 80% reduction of metal in contaminated soil using low grade magnesia. Here 2% of magnesia was used to achieve about 95% reduction in the lead content, Garcıa et al [2004] reported using 10 % of low grade MgO to mobilize 80% of metals (Pb, Zn, Cd, As , Cu, Se and Ni) in contaminated soils.

The maximum amount of lead was extracted from the contaminated soil using the digestion test with 5ml HNO_3 acid in 20ml DI water is shown in Table 5.3.The digestion test followed the procedure described in Section 2.2.4. The acid wash (0.001M HNO_3) of the filter and glass shows that lead was precipitated on the surface and mobilized by adding the magnesia to lead contaminated soil. In addition, the acid wash shows the amount lead which formed on the filter as a result of adding magnesia that was dissolved under acidic conditions. This shows that magnesia was effective at mobilizing the lead.

The addition of magnesia increased the release of Ca, K, Na and Mg, the latter by a considerable amount, see Tables 5.4 and 5.5. The pH levels of contaminated soil were generally lower than uncontaminated soil because of the presence of lead in the soil. In Table 5.2 the results are for a rotary speed of 150rpm, which caused lower extraction of lead and associated elements compared to a rotary speed of 300 rpm, see Tables 5.3 and 5.4.

Table 5.3 Effect of 0.1g of magnesia on lead contaminated soil and effect of acid wash, strength of the contaminating solution, 20,000 mg/l and rotary speed 300rpm

Sample	Pb concentration in final leaching solution (µg/g)	pH
5g lead contaminated soil leached + 50 ml of DI water	47.0	4.6
5g lead contaminated soil leached + 50 ml of DI water	48.7	5.2
5g lead contaminated soil leached + 50 ml of DI water	31.9	4.5
Mean	42.5	4.8
Sd	0.92	-
Acid wash of filter and glassware for contaminated soil	77.5	-
Acid wash of filter and glassware for contaminated soil	78.1	-
Acid wash of filter and glassware for contaminated soil	73.1	-
Mean	76.2	-
sd	2.7	-
5g lead contaminated + 0.1g MgO + 50 ml of DI water	0.88	10.6
5g lead contaminated + 0.1g MgO + 50 ml of DI water	0.71	10.5
5g lead contaminated + 0.1g MgO + 50 ml of DI water	0.66	10.7
Mean	0.75	10.6
Sd	0.01	-
Acid wash of filter and glassware for contaminated soil + 0.1g Magnesia	531	-
Acid wash of filter and glassware for contaminated soil + 0.1 g of Magnesia	645	-
Acid wash of filter and glassware for contaminated soil + 0.1 g of Magnesia	620	-
Mean	598.6	-
sd	59.9	-

Table 5.4 Effect of 0.1g of magnesia on lead contaminated soils using 50ml of de-ionised water, associated elements and anion release, strength of the contaminating solution 1000mg/l, and rotary speed 300rpm

Sample	pH	Pb (µg/g)	Mg (µg/g)	Ca (µg/g)	Na (µg/g)	K (µg/g)	Cl^- (µg/g)	NO_3^- (µg/g)	SO_4^{2-} µg/g)
5g contaminated soil leached with 50 ml of DI water	5.0	34	22.3	141	N/D	13.0	16.7	613	15.3
5g contaminated soil leached with 50 ml of DI water	5.5	34	17.1	137	N/D	17.2	5.5	582	22.1
5g contaminated soil leached with 50 ml of DI water	5.7	39	15.3	130	N/D	23.0	9.3	865	24.7
Mean	5.4	35.6	18.3	136		17.7	10.4	686.6	20.7
sd	0.3	2.8	3.6	5.5		5.2	5.6	155	4.8
5g contaminated soil + 0.1g Magnesia leached with 50 ml of DI water	10.6	0.8	399	210	4.8	9.9	12.2	792	160
5g contaminated soil + 0.1g Magnesia leached with 50 ml of DI water	10.5	N/D	375	216	5.2	10.6	11.72	553	199
5g contaminated soil + 0.1g Magnesia leached with 50 ml of DI water	10.7	N/D	381	213	4.92	10.2	9.9	745	304
Mean	10.6	0.26	385	213.2	4.98	10.2	11.2	697	221
sd	0.1	-	12.4	3	0.2	0.3	1.2	126.6	74.5
5g uncontaminated soil leached with 50 ml of DI water	6.9	N/D	N/D	N/D			5.1	128	7.7
5g uncontaminated soil leached with 50 ml of DI water	6.9	N/D	N/D	N/D			6.0	132	11.3
5g uncontaminated soil leached with 50 ml of DI water	6.9	N/D	N/D	N/D			5.5	121	9.6
Mean	6.9						5.5	127	9.5
Sd	0						0.4	5.3	1.7

N/D. None detected , negative value ,below detect limit.

5.2.2 The effect of leaching with solutions of different pH levels on release of lead and other elements

The effect of pH level of leaching fluid on the release of lead from contaminated soil alone and contaminated soil treated with MgO was investigated using three leachants, see Table 5.5.

Table 5.5 Effect of 0.1g of magnesia on lead contaminated soils with variation in pH with HNO_3 as leaching fluid of the contaminating solution 1,000mg/l, and rotary speed 300rpm. Concentration of metals leached out is given in µg/g

Leaching fluid	Sample	pH	Pb (µg/g)	Ca (µg/g)	Mg (µg/g)	Na (µg/g)	K (µg/g)
50ml DI water	5g Contaminated soil	5.4	37.6	180	19	5.4	17
	0.1g Magnesia + 5g contaminated soil	10.4	7.8	190	250	2.3	17
50ml of 0.1M HNO_3	5g Contaminated soil	1.2	858	2600	280	5.0	22
	0.1g Magnesia + 5g contaminated soil	1.2	531	2200	24000	9.3	20
50ml of 0.01M HNO_3	5g Contaminated soil	2.2	744	2400	270	4.0	20
	0.1g Magnesia + 5g contaminated soil	9.4	1.1	1350	3050	5.4	30

At low pH levels (1.2) the leaching solution gave the highest release of lead and associated elements. This was achieved using 2% by weight of magnesia as stabilizer. 858µg/g was leached from lead contaminated soil with 50ml 0.1M HNO_3. The maximum release of lead and Ca took place with no added MgO. In general, increased amounts of metal are released with decrease in the pH value. With increasing pH the metal solubility decreased to almost non-detectable levels which could be attributed to metal precipitation as hydroxides, as observed by Jing et al., [2004].

$$2Pb\,(s) + O_2(g) + 2H_2O\,(l) \longrightarrow 2Pb\,(OH)_2\,(s)$$

For lead ,the addition of magnesia reduced the concentration of lead in the leachant in all three cases. It can be seen that the reductions in Pb release obtained by adding the magnesia were 79% for DI water (pH=10.4), over 99% for 50ml DI water with 0.01M HNO_3 (pH=2.2), and 38% for 50ml DI water with 0.1M HNO_3 (pH=9.4). However the magnesia acted as a buffer to increase the pH level from 2.2 to 9.4.(Table 5.5). Similar results have been reported by Smith [1996]. A similar trend was seen for Ca [Garcia et al. 2004] reported that MgO act as buffer between pH 9-11.

The amount of Mg release increased to 2400 µg/g when the magnesia was added since it contained 87% MgO, (see Table 5.1).

The following equation describes the use of HNO_3 as a leaching fluid [Harrison et al., 2008]:

$$Mg(OH)_2 + 2HNO_3 \longrightarrow Mg(NO_3)_2 + 2H_2O$$

Morgan et al., [1979] reported similar results using $Mg(OH)_2$ which reacted with HCl. From Table 5.5 it can be seen that maximum release for lead was obtained using a leaching solution of pH level 1.2. However from Tables 5.2, 5.3 and 5.5 it can be seen the release and solubility of Mg is controlled by the rise of pH to 9.4-10.4. where there was a little release of Ca, Na and K.

Chimenos et al., [2000] and Garcia et al., [2004] are in general agreement with this trend of results and reported that leaching of metal is pH dependent in the pH range 9-11, in this study the pH of magnesia treated soils were 9.4-10.5.

5.2.3 The effect of magnesia on soils contaminated with a mixture of metals

Table 5.6 shows the effect of the addition of magnesia to contaminated soil to which had been added 50ml of a solution containing 1000mg/l of a mixture of heavy metals (Pb, Zn, Ni, Cd, Cr and Cu) in DI water, for details of the contamination process see Chapter Two 2.2.3. The leaching batch tests were conducted for 2 hours on a platform shaker. The S/L ratio was 1:10 and the leaching fluid was 50ml of DI water. The treated soils had an average pH of 7.3 and for these the concentration of lead was almost undetectable. The average release of SO_4^{2-} was 24.7µg/g, Cl^- was 10.5µg/g and the highest average release

was for NO_3^-, over 12378µg/g. The initial values were 15.5µg/g for Cl^-, 11710µg/g for NO_3^-, 28.1µg/g for SO_4^{2-}. See Table 5.4 for amounts of Cl^-,NO_3^- and SO_4^{2-} in uncontaminated soils. Table 5.6 clearly shows that magnesia has reduced the leaching of metals in contaminated soils to below the limit of detection of the inductive coupled plasma (AES) technique. Similar findings were reported by Rotting et al., [2006] who used caustic MgO to remediate the mixture of metals (Fe, Cu, Cd, Zn in waste water system and Garcia et al [2004] who used low grade magnesia to remediate the mixture of metals (Pb, Zn, Cu, Mn, Sn, Cr, Ni, V, Al, Fe,As, Se, Sb, Ca and Cd) from soils.

5.2.4 The digestion test for mixture of metal contaminated soils.

The maximum extraction of Pb, Cd, Cr, Cu, Ni and Zn obtained for 1g of contaminated soil using the total digestion acid test with 5ml of HNO_3 and 25ml of DI water on are shown in Figure 3.4 in chapter 3.

5.2.5 The effect of magnesia on a lead contaminated solution

The effect of adding magnesia to different concentrations of lead in solution 500, 1000 and 20000mg/l was investigated; see Tables 5.7, 5.8 and 5.9. The pH value of supernatant was increased to be compatible with removal of the lead from solution and the high release of magnesia. The levels of NO_3^- shown in Table 5.9 were the highest (890mg/l) because of the solubility of lead nitrate, $Pb(NO_3)_2$. There were only small amounts of SO_4^{2-} (0.5mg/l) and Cl^- (0.5 and 2.9mg/l), because no sulphate or chlorine are present in magnesia.

Table 5.6 Effect of magnesia on soil contaminated with (Pb, Zn, Ni, Cd, Cu, Cr and Cu), leached with 50 ml of water

Sample	pH	Pb (µg/g)	Zn (µg/g)	Ni (µg/g)	Cd (µg/g)	Cr (µg/g)	Cu (µg/g)	Cl^- (µg/g)	NO_3^- (µg/g)	SO_4^{-2} (µg/g)
Metals contaminated soil + 50 ml of DI water	4.0	857	880	905	987	881	927	17.1	0.03	20.7
Metals contaminated soil + 50 ml of DI water	4.0	883	1065	1084	1193	902	1107	17.0	18751	33.7
Metals contaminated soil + 50 ml of DI water	3.9	912	946	975	1056	933	980	11.2	16370	30.0
Mean	3.9	884	964	988	1079	90.5	1005	10.3	14418	24.8
Sd		27.6	93.7	90.2	104.9	26.2	92.5			
Metals contaminated soil + 0.1g of MgO + 50ml of DI water	7.5	N/D	N/D	N/D	N/D	N/D	N/D	10.4	10127	21.1
Metals contaminated soil + 0.1g of MgO + 50ml of DI water	7.3	N/D	N/D	N/D	N/D	N/D	N/D	10.1	11334	23.5
Metals contaminated soil + 0.1g of MgO + 50ml of DI water	7.2	N/D	N/D	N/D	N/D	N/D	N/D	11.2	15674	29.5
Mean	7.3							10.6	12378	24.7
Sd	0.2							0.50	2917	4.30

N/D = no detected, negative value, below detect limit.

Table 5.7 The effect of 0.1g of magnesia on lead solution, and change of the pH in the final solution with the effect of the acid wash, strength 500mg/l (n=3)

Sample	Concentration of Pb (mg/l) in final solution	pH
50ml of 500mg/l of Pb solution	498	3.9
50ml of 500mg/l of Pb solution	495	4.0
50ml of 500mg/l of Pb solution	496	4.0
Mean	496	4.0
sd	1.55	0.05
50ml of 500mg/l of Pb solution + 0.1g Magnesia	0.76	10.2
50ml of 500mg/l of Pb solution + 0.1g Magnesia	2.5	11.0
50ml of 500mg/l of Pb solution + 0.1g Magnesia	1.1	10.4
Mean	1.45	10.5
sd	0.9	0.41
acid wash		
500mg/l + 0.1g Magnesia(filter + glass)	398	
500mg/l + 0.1g Magnesia (filter + glass)	392	
500mg/l + 0.1g Magnesia (filter + glass)	393	

The effect of magnesia on the 500mg/l lead solution was determined by adding the same amount of magnesia as used to treat contaminated soil in Section 5.2. The mixture was shaken for two hours and filtered using Whatman grade 542 filter paper. The eluate was assessed using ICP, and the pH was measured. Varied concentrations of lead were used: 50,100, 500, 1000 and 20,000 mg/l. The result of adding 0.1g of magnesia to 50ml of lead solutions of strengths 100, 500, 1000mg/l on the pH level was to raise it from 4.0 to 10.5, see Tables 5.7, 5.8 and 5.9 respectively. For 1000mg/l of Pb solution, there was a major increase in the amount of Mg (to about 317mg/l) which caused an increase of pH to about 10.3 causing a decrease of Pb in the final solution to almost zero(see table5.4). The pH increased to 9.7 with the addition of 0.1g of MgO to the solution of strength 20,000mg/l. The resulting concentration of Pb in the final solution was less than 1mg/l (0.56mg/l) which means the reduction was 99%.

Table 5.8 Effect of 0.1g of magnesia on lead contaminated solution and release of the associated elements, and results of acid wash concentrations found in final solution

Sample	pH	Pb (mg/l)	Mg (mg/l)	Ca (mg/l)	Na (mg/l)	K (mg/l)
50ml of 500mg/l of Pb solution	4.4	497	ND	ND	ND	ND
50ml of 500mg/l of Pb solution	4.3	498	ND	ND	ND	ND
50ml of 500mg/l of Pb solution	4.2	496	ND	ND	ND	ND
Mean	4.3	497				
Sd	0.1					
50ml of 500mg/l of Pb solution + 0.1g Magnesia	10.2	0.76	79	9.49	0.64	0.123
50ml of 500mg/l of Pb solution + 0.1g Magnesia	11.0	2.50	80	10	0.7	0.189
50ml of 500 mg/l of Pb solution + 0.1g Magnesia	10.3	1.10	80.5	9.9	0.68	0.155
Mean	10.5	1.45	79.8	9.79	0.67	0.15
Sd	0.1	0.92	0.76	0.27	0.03	0.03
Acid wash		Pb (mg/l)	Mg (mg/l)	Ca (mg/l)	Na (mg/l	K (mg/l)
50ml of 500mg/l of Pb solution + 0.1g magnesia		398	-	-	-	-
50ml of 500mg/l of Pb solution + 0.1g MgO (filter+ glass)		392	-	-	-	-
50ml of 500mg/l of Pb solution + 0.1g MgO (glass)		393	-	-	-	-
Mean						
Sd						

N/D = None detected

Table 5.9 Effect of 0.1g of magnesia on lead solution, strength of 1000mg/l concentrations found in final solution

Sample	pH	Pb (mg/l)	Mg (mg/l)	Ca (mg/l)	Na (mg/l)	K (mg/l)	Cl^- (mg/l)	$NO3^-$ (mg/l)	SO_4^{2-} (mg/l)
0.1g of Magnesia + 1000mg/l Pb solution	9.9	N/D	353	42.6	1.86	N/D	0.405	968	4.85
0.1g of Magnesia + 1000mg/l Pb solution	10.4	N/D	310	51.8	2.34	0.186	0.606	837	1.16
0.1g of Magnesia + 1000mg/l Pb solution	10.3	N/D	288	72.1	3.16	N/D	0.506	863	1.78
Mean	10.3		317	55.5	2.45	0.186	0.500	890	2.59
Sd			33.1	15.1	0.65	0.149	0.105	69.3	1.97

N/D=no detected

The mechanism of the reaction of magnesia with water that produced the higher alkalinity is:

$$MgO + H_2O \longrightarrow Mg(OH)_2$$

The extent to which Mg $(OH)_2$ may occur in the water is a complex reaction, Harrison [2008] suggested the following:

$$Mg(OH)_2.nH_2O \longrightarrow Mg(OH)_2 + nH_2O$$

Alternatively alkaline material has the capacity to buffer the pH in solution, by increasing the pH of the contaminated solution to 9-11, Garcia et al., [2004] and Rotting et al [2008] are in agreement with this pH value, which can remove heavy metals almost completely from water.

5.2.6. Effect of magnesia on solution containing a mixture of metals

The test for the effects of magnesia on a mixture of metals in solution was carried out in the same manner as for the lead in solution, and preparation procedure is as described in Section 2.2.2. All the metals were added to the solution as nitrate salts, e.g lead nitrate $Pb(NO_3)_2$. Table 5.10 shows the result of adding 0.1g MgO to the 100mg/l metals solution containing Pb, Zn, Ni, Cd, Cr, Al, Cu and Fe. When using OPC or lime the pH was controlled by the solubility of portlandite, Ca(OH), but when using magnesia the pH is controlled by solubility of MgO [Garcia et al 2004].The pH factor of the leachant plays a major role in the stabilization of mixtures of metals. When any metallic element is immersed in a solution there is a pH value for the solution at which that element begins to be soluble, below that pH level the metal is insoluble [Conner and Hoeffner, 1998a]. For instance pH 4 the lead is not soluble but at 6.5 or more lead is soluble, adding magnesia to metal solution gave the final pH 8.4. When the pH level of the solution is between 8 – 8.7 the magnesia was very effective at reducing the amounts of all of the metal elements in the mixture solution to below the detection limit(see Table 5.10). The largest mean releases of associated elements were Mg, 397mg/l and Ca, 9.3mg/l while both Na and K were below 1mg/l. The precipitation of the metals was on the surface of the glass and filter since they were not in the eluted solution. Dissolving the precipitated material using an acid wash shows most metals accumulated on the filter paper, see

Tables 5.8 and 5.10. Adding acid washing is important to prove that the metals were removed from the solution and precipitated on the surface.

Table 5.10 Effect of 0.1g of magnesia on mixture of metals in solution with Pb, Zn, Ni, Cd, Cu, Cr and Cu, strength of the contaminating solution 1000mg/l

Sample	pH	Zn (mg/l)	Pb (mg/l)	Ni (mg/l)	Cd (mg/l)	Cr (mg/l)	Al (mg/l)	Cu (mg/l)	Fe (mg/l)	Mg (mg/l)	Ca (mg/l)	Na (mg/l)	K (mg/l)
100 mg/l metals solution	2.9	101.2	100.6	97.0	101.7	98.9	99.7	102.9	93.2	N/D	N/D	N/D	0.04
100 mg/l metals	2.8	106.2	106.9	103.5	99.0	101.4	100.2	105.9	95.0	N/D	N/D	N/D	0.01
100 mg/l metals	2.8	102.0	103.0	101.0	100.0	99.9	100.0	103.0	97.0	N/D	N/D	N/D	N/D
Mean	2.8	103.1	103.5	100.5	100.2	100.1	100.0	103.9	95.1	N/D	N/D	N/D	0.02
Treated samples													
0.1g of MgO +100mg/l metals solution	8.0	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	399.3	8.57	0.81	0.49
0.1g of MgO +100mg/l metal	8.8	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	407.3	9.64	0.30	0.93
0.1g of MgO +100mg/l metal	8.3	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	385.8	9.94	0.30	0.62
Mean	8.4	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	397.5	9.38	0.47	0.68
SD	0.39	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	10.8	0.72	0.29	0.22
acid washing	pH	Zn (mg/l)	Pb (mg/l)	Ni (mg/l)	Cd (mg/l)	Cr (mg/l)	Al (mg/l)	Cu (mg/l)	Fe (mg/l)	Mg (mg/l)	Ca (mg/l)	Na (mg/l)	K (mg/l)
0.1g of magnesia + 100mg/l metals solution	-	125.1	139.2	118.0	92.2	145.5	153.8	157.5	139.1	-	-	-	-
0.1g of magnesia + 100mg/l metals	-	101.6	118.9	60.3	47.4	121.1	194.6	139.4	159.2	-		-	-
0.1g of magnesia + 100mg/l metals	-	129.2	132.2	128.0	131.5	141.6	148.8	156.6	136.5	-	-	-	-

N/D=not detected

5.3 Characterisation of Precipitated Materials

Further investigation was required to explain the chemical reactions which occurred as a result of conducting the leaching test and contact between the stabilized materials and contaminant either in solution or the soils. The most useful chemical analytical tools in this field are Fourier transform infrared (FTIR), Raman spectroscopy, X-ray diffraction (XRD) and X-ray photo spectroscopy (XPS).

5.3.1 FTIR investigations of lead contaminated soils and solution

A similar procedure to that described in Sections 3.5 and 4.3 was followed when examining the effect of magnesia on Pb contaminated soil and Pb contaminated solution. Figure 5.1 shows the FTIR spectra for magnesia with lead (A) compared to magnesia only (B). The two spectra differ only in the slight but clearly discernible drop for magnesia stabilized lead at 2377cm^{-1}, and a strong peak at 3696cm^{-1}. According to Barnett et al[2002]. (see Table 5.11), this drop at 2377cm^{-1} can be assigned to the stretching of O-H in $Ca(OH)_2$ and is attributed to Pb-OH-$Ca(OH)_2$. According to Mercy et al., [1998] that means hydrocerussite $Pb(OH)_2.(PbCO_3)_2$ is formed as result of mixing the magnesia with the Pb solution. The peak at 399cm^{-1} is assigned to V_2.Si-O, which can be attributed to Pb–Si-O compounds, the presence of which is confirmed by other techniques used in this study; ESEM, Raman and XRD, see Sections 5.7.2, 5.7.3 or 5.7.4.

The FTIR spectra for soil contaminated with lead and the contaminated soil treated with magnesia, (see Figure 5.2), show a peak at 3419.4cm^{-1}, which was assigned to V_1 and V_3 of O-H, which means presence of hydrogen-oxygen vibration plus one free, the vibration frequencies v_1, v_2 and v_3 for differently strong bases in water, that indicates the presence of Pb-OH, which agrees with Namasivayam and. Ranganathan [1995]. The hydrogen-bond at 3400cm^{-1} and the strong peak at 1105.9cm^{-1} are, according to Barnett et al., [2002], assigned to $V_3.SO_4^{2-}$ and can be attributed to Pb SO_4^{2-}.

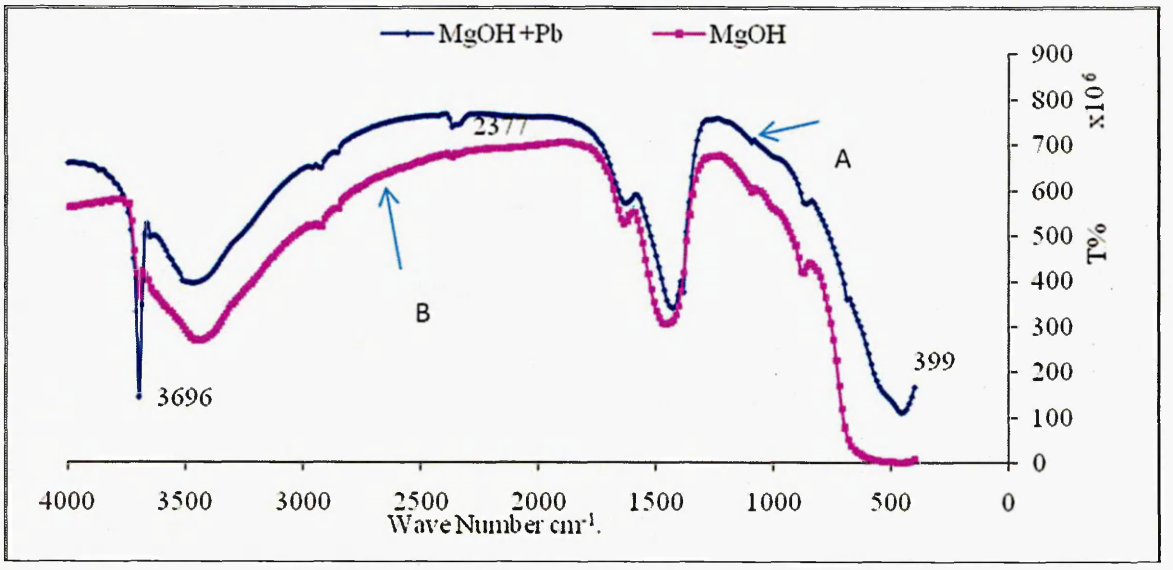

Figure 5.1 FTIR plot of effect of magnesia on lead contaminated solution, (A)- Spectrum for magnesia stabilized lead solution, (B)-Spectrum for magnesia with no lead in solution

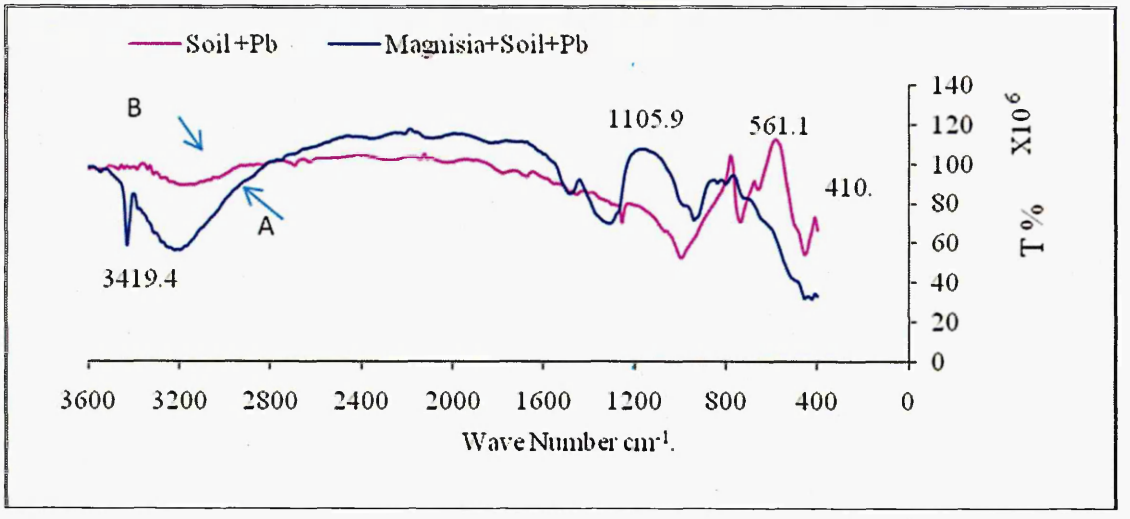

Figure 5.2 FTIR for soil contaminated with Pb before and after treatment with magnesia, (A) -Spectrum for lead contaminated soil, and (B)- Spectrum for contaminated soil treated with magnesia

Table 5.11 Principal FTIR frequency bands in hydrated Portland cement (Barnett et al [2002] compared with results in this study

Wave number (cm^{-1})	Assignment	Soil+ Pb + Magnesia In this study	Magnesia +Pb solution In this study
3645	stretching O-H of Ca(OH)2	3600	3416
3100-3400	symmetric and asymmetric stretching (Vl and V3 of O-H	3419	
1650	Deformation(V2)H_O_H		2377
1480	$V3.CO3^{2-}$	1105	
872	$V2.CO3^{2-}$		
712	$V4.CO3^{2-}$	810	
970	stretching Si-O(V3) (in polymeric unit of $SiO4^4$		
925	(stretching Si-O(V3) (in non-hydrated cement)		
			399
452	V2.Si-O	410	
1115	$V3.SO_4^{2-}$	1105	

5.3.2 Raman Spectroscopic Analysis of lead contaminated soils and solution

Mestl et al[1993] described how with Raman spectroscopy the penetration depth of the radiation is much less than its wavelength, and thus while Raman spectroscopy is successful at characterising surfaces that include metals, it does not give the spectra of the metals themselves.

The results of the Raman Spectroscopic analysis carried out on 0.1g of magnesia treated lead solution and lead contaminated soils are shown in Figures 5.3 and 5.4. The concentration of lead was 20,000 mg/l to enable the Raman technique to detect the lead and magnesia. For the magnesia treated lead solution, there was a clear and large peak at $1040cm^{-1}$, this is substantially different from the spectrum for magnesia alone, which had no comparable peaks. A trio of (relatively) very small peaks were noticed at $180cm^{-1}$, 230 cm^{-1} and 687 cm^{-1}. The only peak in Figure 5.3 is at 1040 cm^{-1} and can be referred to $PbCO_3$. Mestl et al [1993] reported that the peak at $1097cm^{-1}$ arises from surface carbonate groups. Bersani et al.[2008] reported lead carbonate peaks at $681cm^{-1}$ and 280 cm^{-1}, and plumbonacrite, $Pb10(CO_3)6O(OH)$, peaks at $460cm^{-1}$.

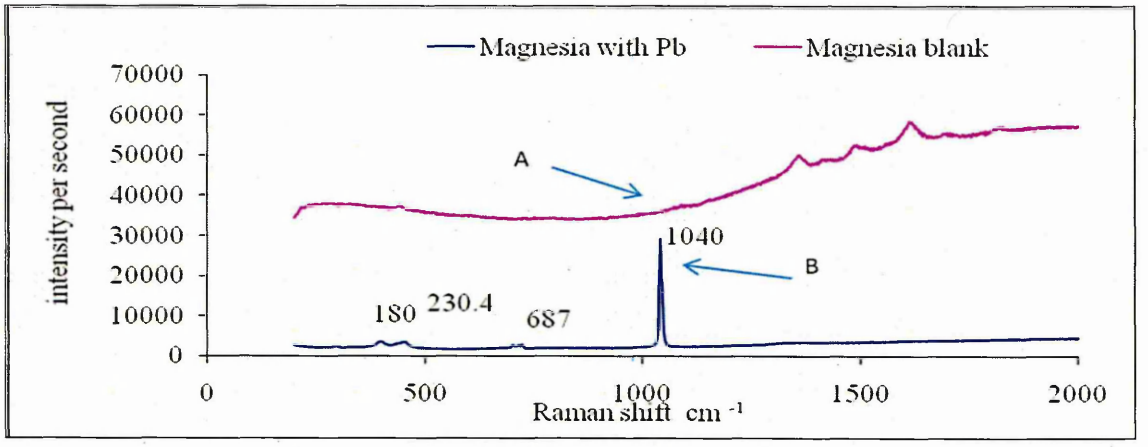

Figure. 5.3 Raman spectra for: (A) 0.1g magnesia in 50ml DI water, (B) 0.1g of magnesia in 50ml of lead solution of strength 20,000 mg/l

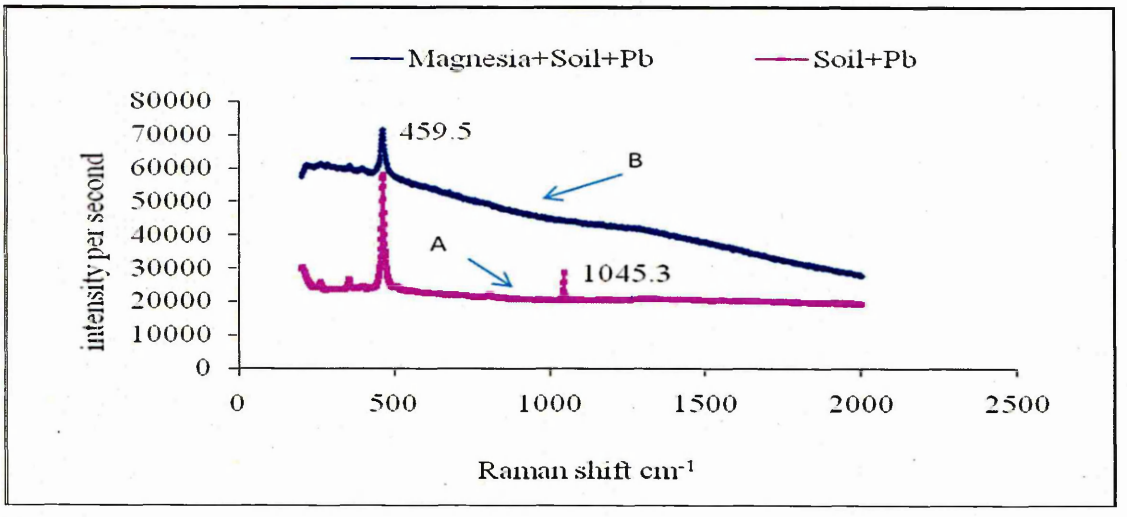

Figure 5.4 Raman spectra for: A - soil of mass 5g contaminated with 20,000mg/l of lead, (B) – as (A) but treated with 0.1g of magnesia.

5.3.3 X-ray Diffraction Investigation

The XRD measurements were made for magnesia stabilized lead solution and magnesia in DI water with no lead. Figure 5.5 shows the results obtained and also for lead contaminated soil treated with magnesia (see Figure 5.6), where few peaks were detected because no curing had occurred between the contaminated soil and the magnesia. Figure 5.5 shows peaks at 13.84°, 16.35° and 29.4°, according to the Cambridge Chemical structure database these are attributable to PbMg(V207). One peak at 22.44° can be attributed to Mg_2Pb (magnesium plumbide). The peaks occurring at 33.33° and 49.3°were both assigned to PbO_2 (lead peroxide), and two other peaks at 44.3° and 46.242° were assigned to magnesium plumbide (Mg_2Pb-[FM3-M]), (see also Faessler and Kronseder, [1999]).

In this study MgO was seen with the 38° peak, see Figure 5.5, also reported by Okazaki et al., [2008] who used XRD to investigate magnesia stabilized solutions. However, Cotina et al., [2003] reported hydrocerussite, $Pb_3(CO_3)_2(OH)_2$, was formed as result of the reaction of $Pb(OH)_2$ with the atmospheric CO_2 when there was no lead detected in the solution . The presence of PbO_2 was identified in one strong peak at 49.3^0 and $PbSO_4$ at 33.4^0, both of which have been confirmed by Lee et al., [2005], (see Figure 5.5).

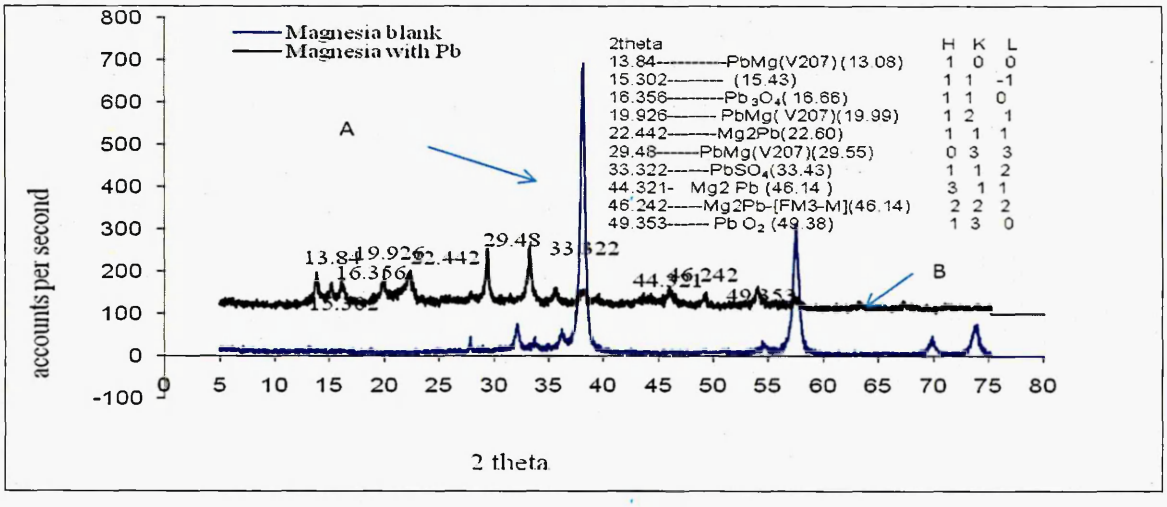

Figure 5.5 X-Ray diffractions for magnesia stabilized lead: (A)- Spectrum for magnesia in DI water,(B)- Spectrum for magnesia stabilized lead solution.

$PbSO_3$ or Pb SO_4 or $PbCO_3$-S could be responsible for the peaks at 20° and 29.5° since the other techniques used (SEM, Raman, FTIR, XPS) confirmed those compounds to be presented in the samples. Moreover, the peak at 16.66° is due to Pb_2O_3 as confirmed by Dinnebier, et al., [2003]. There is a peak at 15.34° but a literature search did not define any substance which could be responsible. However, it should be mentioned that little research has been done into identifying magnesia for stabilization purposes. Nevertheless, according to Garcica et al [2004] the following compounds were identified using XRD after magnesia was added to metal contaminated soil: brucite ($Mg(OH)_2$; PDI 7-0239), magnesite ($MgCO_3$; PDI 8- 0479), dolomite ($CaMg(CO_3)_2$; PDI 36-0426), calcite ($CaCO_3$; PDI 5-0586) and quartz (SiO_2; PDI 33-1161) all of which were present as major mineralogical phases in LG-MgO used in his investigation. PDI is the crystallization dimensions in the solid material, which is a measure of the distribution of molecular mass in a given polymer sample, the polydispersity index (PDI).

A range of peaks 35°-40° and again at 55-60° were observed for magnesia in DI water, see Figure 5.5 and are assigned to $Mg(OH)_2$. It is known that the periclase–brucite transformation according to Wang et al., [2009] in the presence of water or the hydroxyl groups .[Lingaiah et al 2001].

For investigation of contaminated soil and contaminated soil treated with magnesia few peaks were identified using XRD for magnesia stabilized soil. The reason for this is that there was no physical binding between the magnesia and the contaminated soil. According to Faessler and Kronseder, [1999] and Jahn and Martonak [2009] and the Cambridge mineral data base: for contaminated soils treated with magnesia, (see Figure 5.6), the peaks at 21.8° theta are assigned to Mg_2Pb-[FM3-M], the peak at 16.08 ° theta is assigned to -Mg_5O_4 $(OH)_2$-[P3-M1], and the peak at 34.13° theta is assigned to protoenstatite-$Mg(SiO_3)$-[PBCN].

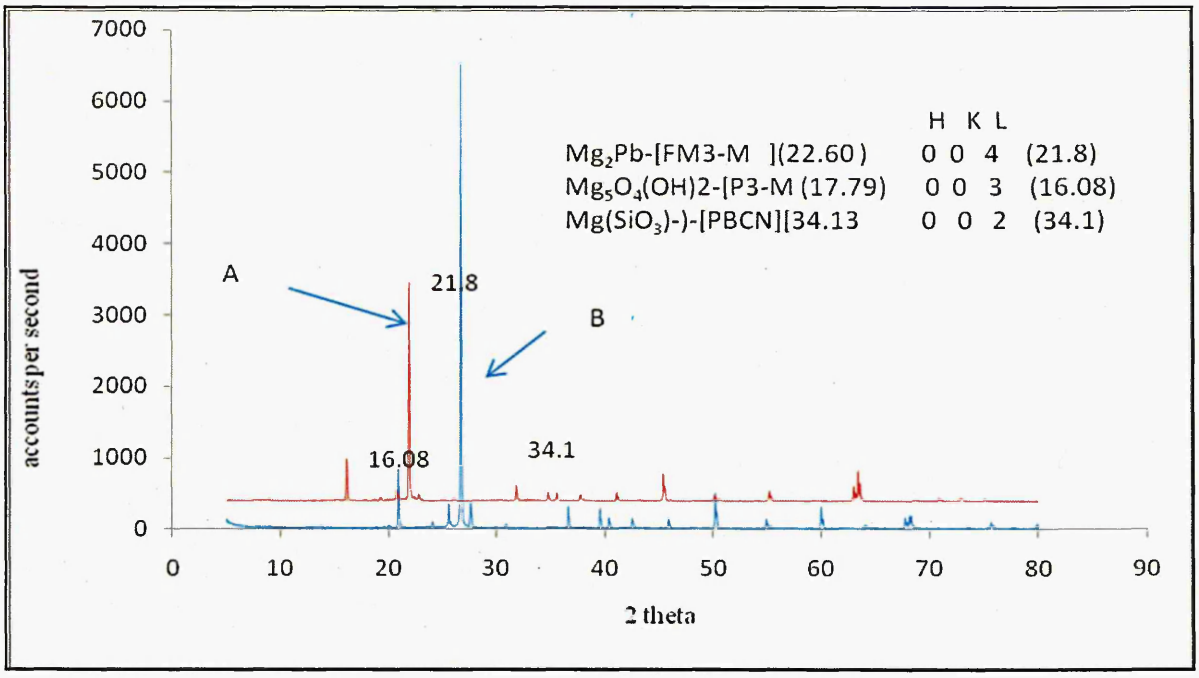

Figure 5.6 X-Ray diffractions for lead contaminated soils: (A) Spectrum for magnesia treated soils, (B) Spectrum for lead contaminated soils

5.3.4. Environmental scanning electron microscope

The ESEM observations were conducted on treated and non-treated samples. The object of this scan was to investigate the presence of lead in certain precipitated materials resulting from the chemical reactions, which occurred after adding the magnesia to the lead solution and lead contaminated soils. Figures 5.7a and 5.7b show the presence of lead in the magnesia treated contaminated soil. Figure 5.8 clearly shows the precipitated of lead as spherical particles in the surface material precipitated onto the filter, which supports the finding of the ICP measurement, that lead was mobilized on the surface of the magnesia. In Figure 5.7b the results of the EDX investigation show the lead in samples associated with Mg, Si Al, O, and K. Taub et al., [2008] used the same technique to investigate metals in soil remediation.

The presence of Al, O and Mg in the samples indicate that several compounds may be formed; e.g. bayerite $[Al(OH)_3]$,$Mg_2Al(OH)_7$, $(Mg0.667Al0.333)(OH)_2]$, Rotting et al., [2006] support this conclusion.

The morphology of magnesia was soft calcite and needle shapes as in ESEM. Figure 5.8a shows the lead coated surface of the magnesia; see also Figure 5.8b where EDX shows lead, Mg, and O in the sample, proving precipitation and mobilization of lead by magnesia. This result showing the presence of lead in the target sample (magnesia) confirmed the results obtained by ICP and are also in agreement with the finding of XRD, FTIR and Raman Spectroscopy reported here.

Figure 5.7a ESEM image for Soil treated with magnesia, the lead is a white spherical shape

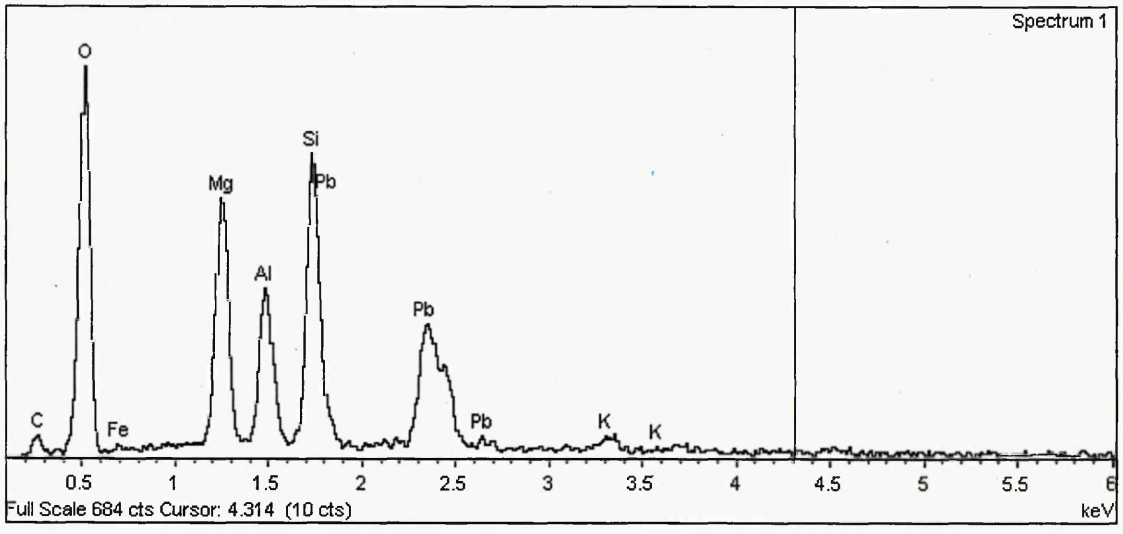

Figure 5.7b EDX map for ESEM image for soil treated with magnesia (Pb and associated elements ,Mg, AL, Si, Fe, C, O ,and K)

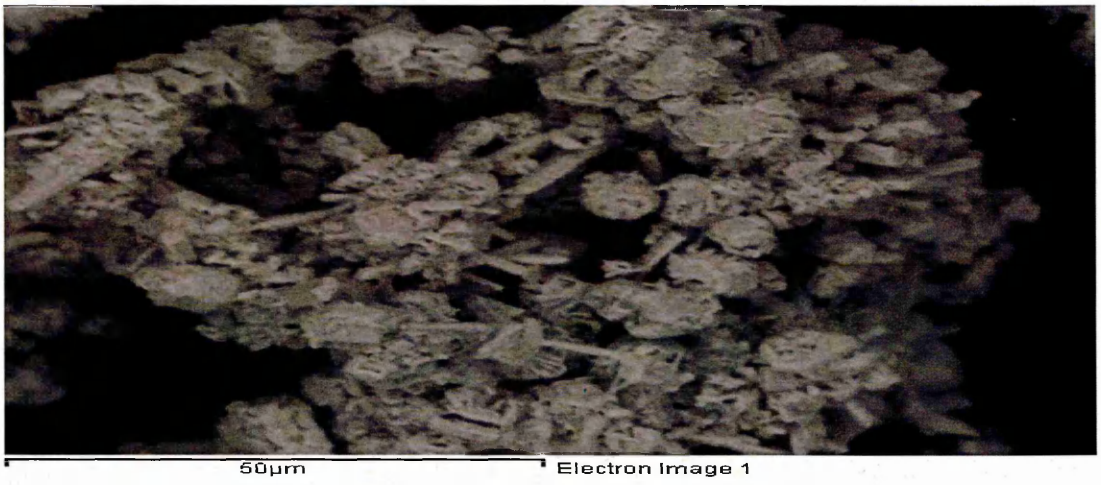

Figure 5. 8a ESEM image for magnesia stabilized lead solution

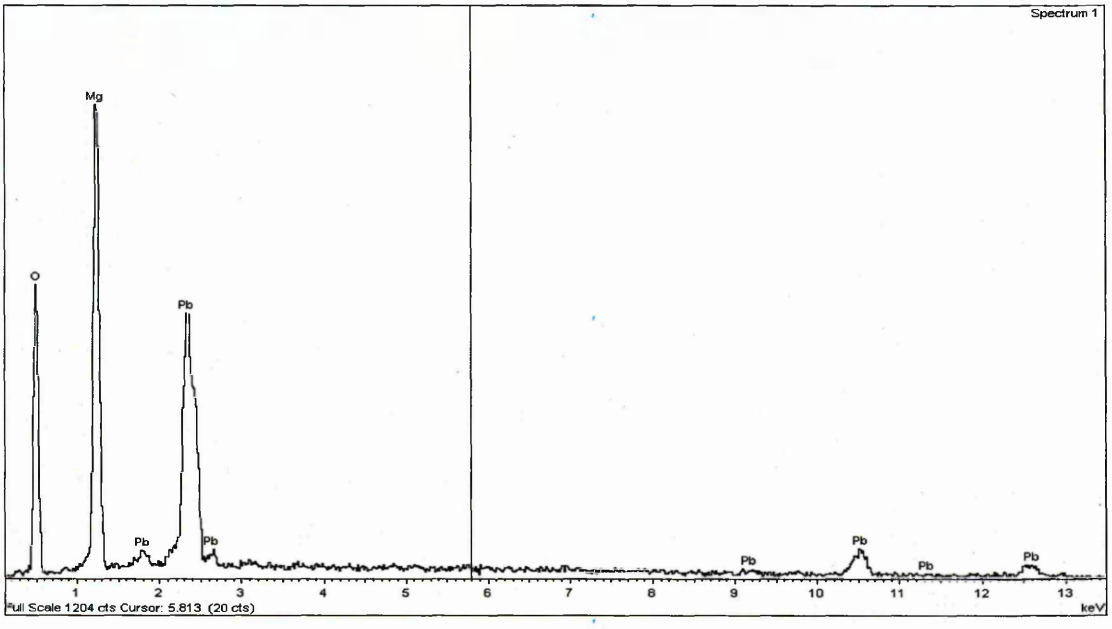

Figure 5.8b EDX for ESEM image for spectrum of magnesia stabilized lead solution, Pb and associated elements (Pb, Mg and O)

5.3.5 X-ray photoelectron spectroscopy investigation

5.3.5.1 The X-ray photo spectroscopy investigation for lead contaminated solution

Figures 5.9 to 5.13 were obtained using XPS on magnesia alone, with no lead solution and 0.1g magnesia stabilized Pb solution strength 20,000 mg/l. Figure 5.11 shows a wide XPS scan on which can be seen a small peak, which was identified as lead 4f. The lead 4f peak is, in fact, naturally shaped as a "doublet" (i.e., has two main peaks separated by 4.7eV) positioned around 140eV with an area of 3.19% of the total occupied by the sample, and is one of the smallest of the peaks listed. Each of the two peaks of the doublet was further made up of separate peaks arising from the various chemical states of lead that were present. Figure 5.12 shows Pb4f at 137.3eV and 142.2eV are attributed to Pb4f7/21 and the peak 142.20eV to Pb4f5/21, (see Figure 5.13). According to Jing et al., [2005] the Pb4f5/21 peak contributed to $PbO_{x\ (x=1or2)}$, $PbSO_3$, and $PbSO_4$or PbO. According to Alexei et al [2004] Lead sulphate defined the peaks from 137.6eV to 143.5eV, the peak at 139eV is classified as Pb-S either $PbSO_3$,$PbSO_2$ (lead hyposulphite), or $PbSO_4$.

The peak of Pb4f7/21at 139eV is shown in wide scan of the samples in Figure 5.12, according to XPS international data, James et al., [2008] and Tao Zhu et al., [1997]. However, a wide scan of magnesia in DI water, Figure 5.11, for magnesia powder did not show any Pb peaks in the region of Pb4f. Figure 5.10 for magnesia in DI water shows the O1s peak occupied 35.9% of the total sample area, Mg2a occupied 34.1%, and both Ca2p and Cls occupied 10% each. Also present is Al2p with 6.7%. These compositions are in agreement with results obtained for chemical oxidizations by XRF, see Table 5.1.

Reduction of Mg and Ca and also O at magnesia stabilized lead solution, see Figure 5.11, can be only explained if those elements were dissolute and soluble during the reaction between the magnesia and lead solution in the presence of water.

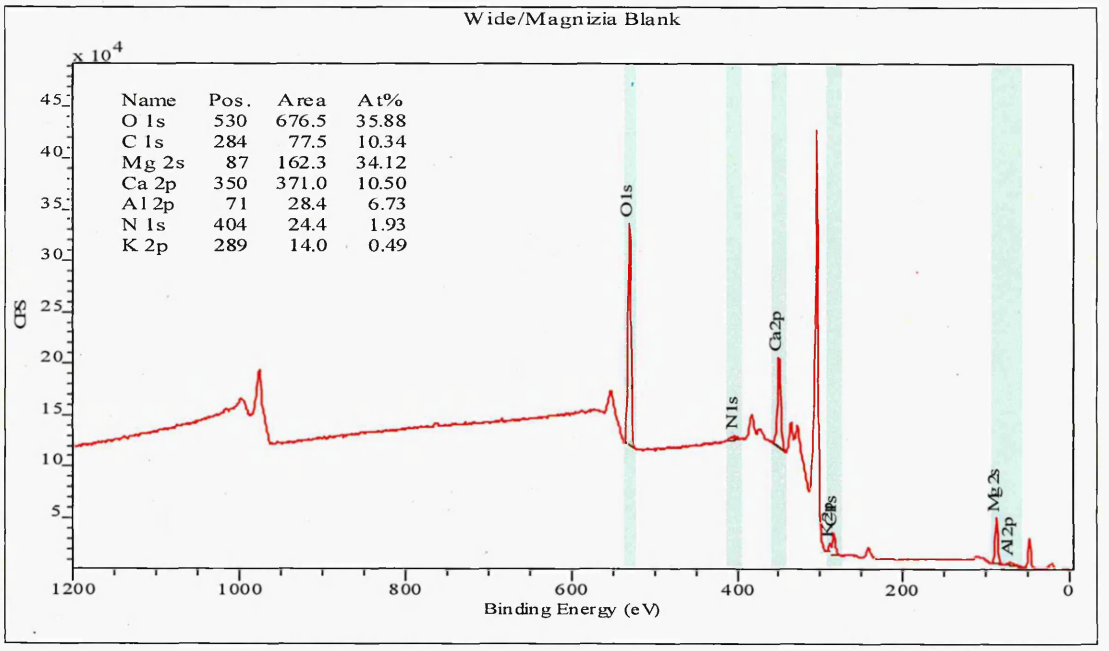

Figure 5.9 Wide scan XPS for 0.1g of magnesia in 50ml deionised water

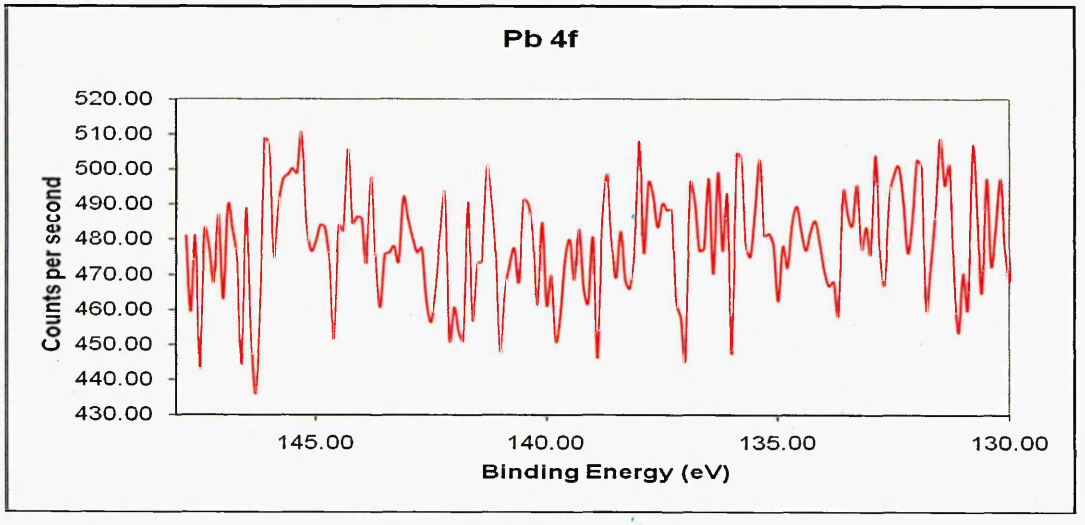

Figure 5.10 Detailed XPS analysis of the spectrum for magnesia powder alone over the region of the lead 4f spectral line

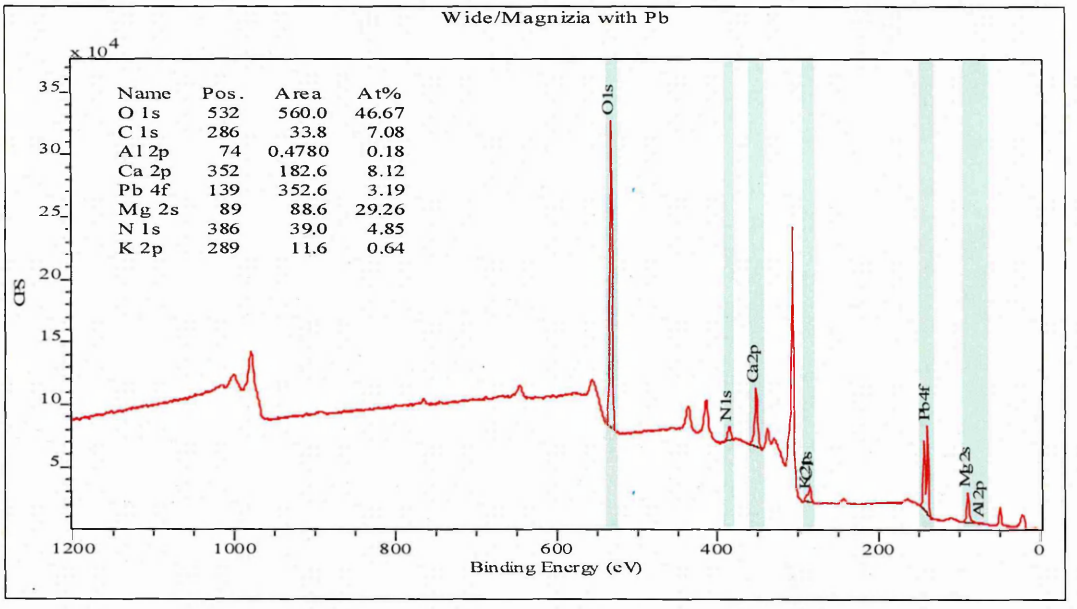

Figure 5.11 Wide scan of XPS spectra for magnesia stabilized Pb solution

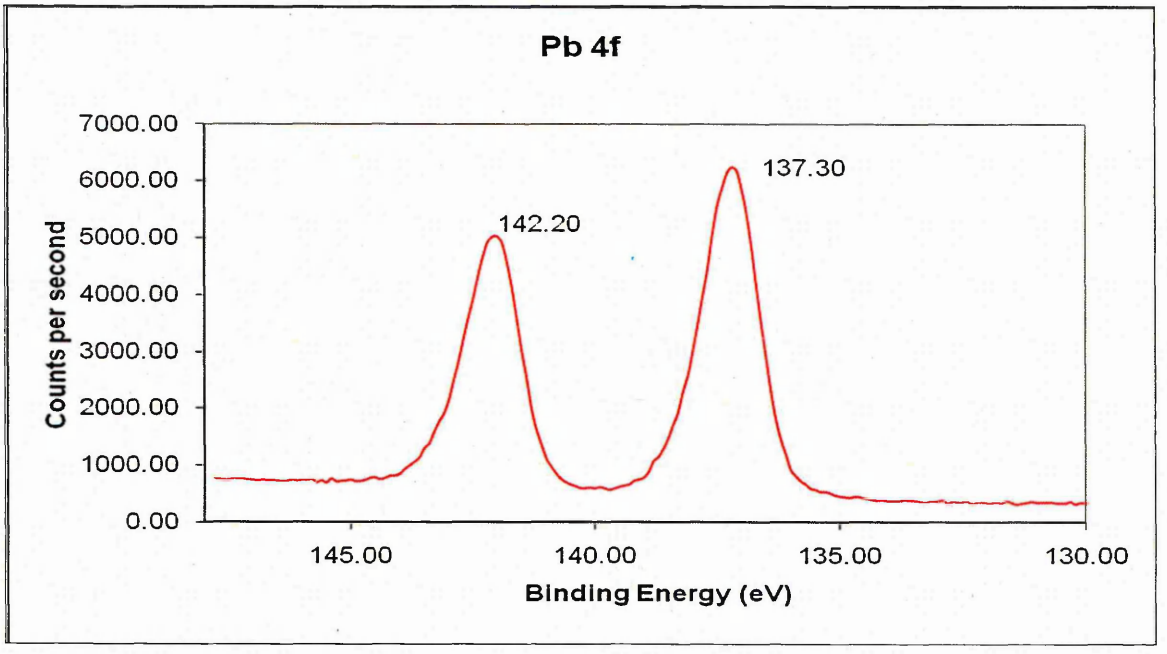

Figure 5.12 Detailed XPS analysis of the spectrum for magnesia stabilized lead contaminated solution, over the region of the lead 4f spectral lines

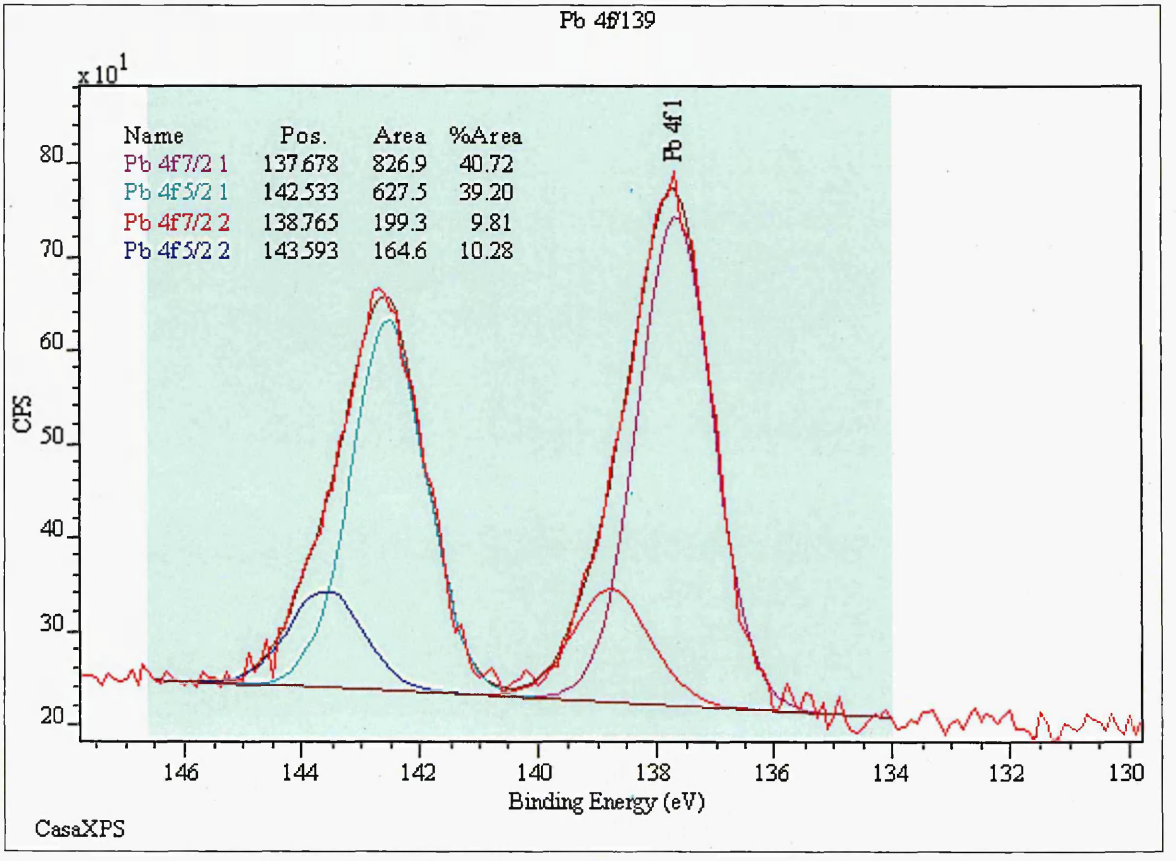

Figure 5.13 Distribution of lead peaks on wide scan by XPS for Pb4f/139

5.3.5.2 The X-ray photo spectroscopy investigation for lead contaminated soil

For the XPS investigation of lead contaminated soil the same procedures were followed as described in Section 2.1.5 for OPC. Figure 5.14 shows the wide XPS scan of magnesia stabilized lead contaminated soil and the lead4f peak is at 136eV with 0.59 %. As can be seen from Figure 5.14, Ols had 48.6%, Mg2s had 19.4 %, C1s had 14.1 %, Si2p had 6.07 %, and Ca2p had 5.8 % and AL2p 2.4 %.

For magnesia in uncontaminated soil, Figure 5.19, the O1s peak was 50%, and there was a greater amount of Si, 10%, where no lead had been identified (see Figure 5.20). Also the Mg in blank sample is 15.8%, while magnesia treated soil is 19% which confirms the results obtained by ICP that there is a release large amount of Mg.

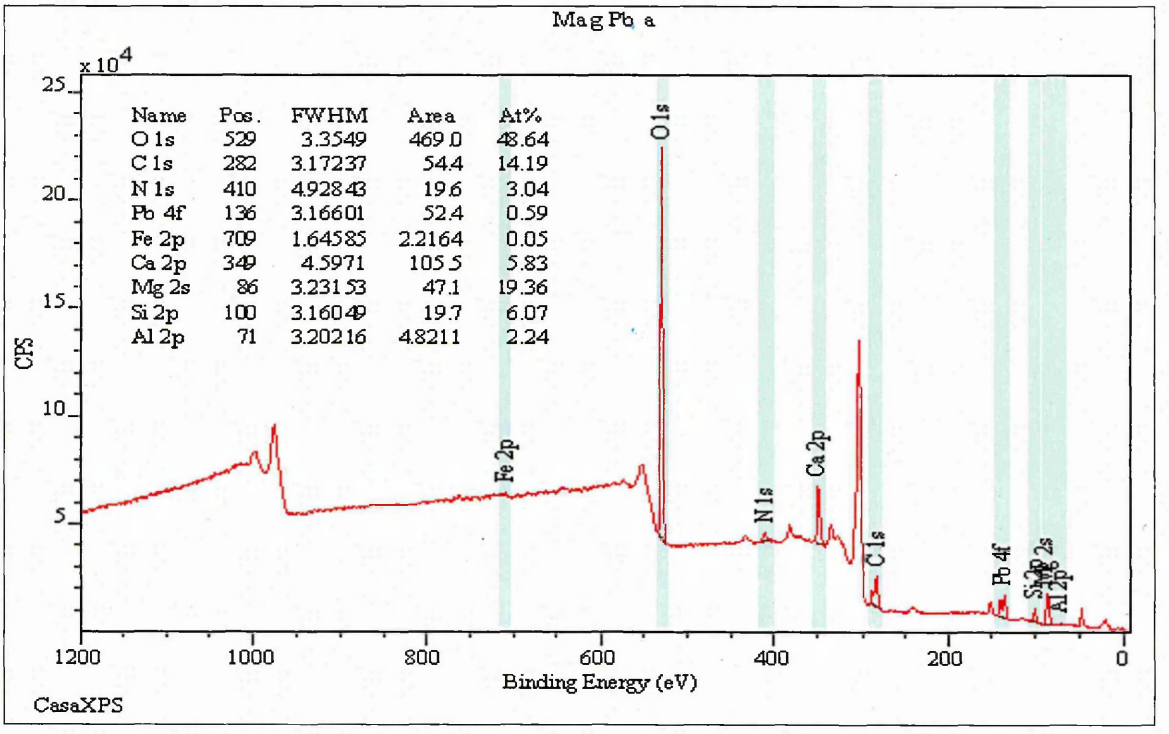

Figure 5.14 XPS wide scan for magnesia stabilized Pb contaminated soil

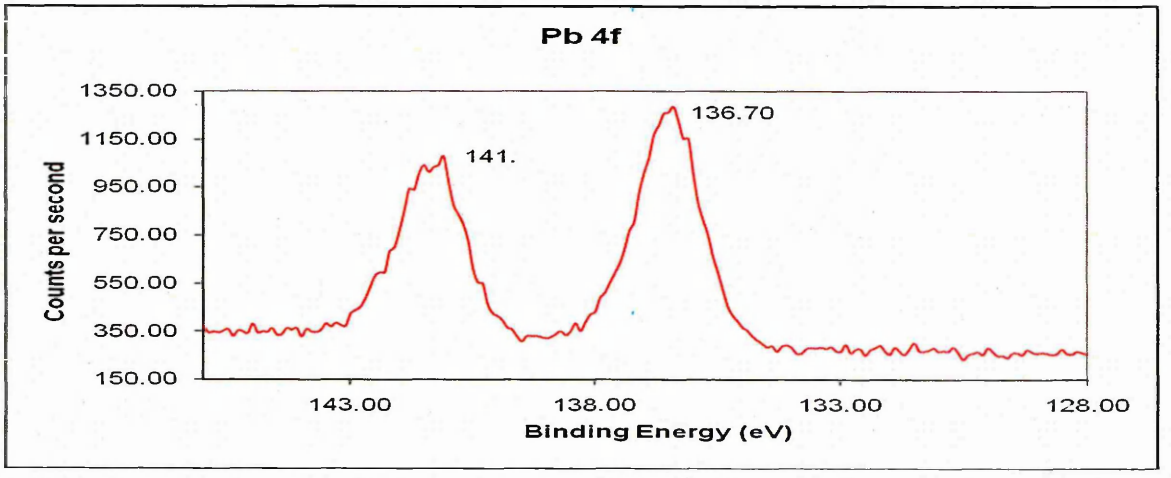

Figure 5.15 Detailed XPS analysis of the spectrum for magnesia stabilized lead contaminated soil, over the region of the lead 4f spectral line

Figure 5.16 shows the XPS wide scan of untreated lead contaminated soil. The position of the lead Pb4f at 136eV can be clearly seen, occupying about 0.91 %. The figure also shows that Ols had 55.6%, Si2p had 20.1 At%, Al2p had 8%, C1s had 7.1%, N1s had 4.7%, Mg2s had 1.5% and Ca2p had 1.2%.

However the peaks 136eV are assigned to Pb4f7 according to the XPS International database and 141eV is assigned to Pb4f5, (see Figure 5.18 and 5.17). After James et al., [2008] the 137eV and the doublet 141eV are assigned to PbO or $PbSO_3$. According to Tao Zhu et al., [1997] the peaks Pb4f are given to PbO or $PbCO_3$, while Mekki [2003] reported and defined the 4Pb4f as due to the formation of PbO_3 and PbO_4. Kanunnikova et al [2004] supported this conclusion and also suggested the possibility of the formation of $PbO\text{-}SiO_2$ since there was Si in the soils. The FTIR and XRD results in Section 5.5.3 are in agreement with these results.

In addition to the above several compounds of lead were formed on the surface of the stabilized treated soil, see Figure 5.19, this confirms the XRD results in this study, see section 5.5.3,which detected several lead compounds formed on the surface.

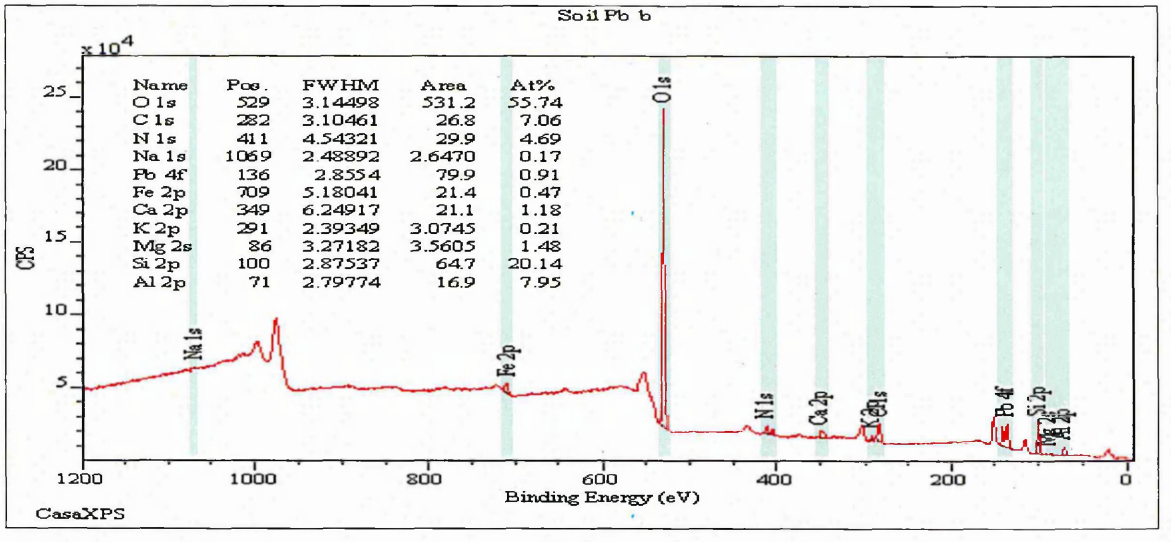

Figure 5.16 XPS wide scan of lead contaminated soil

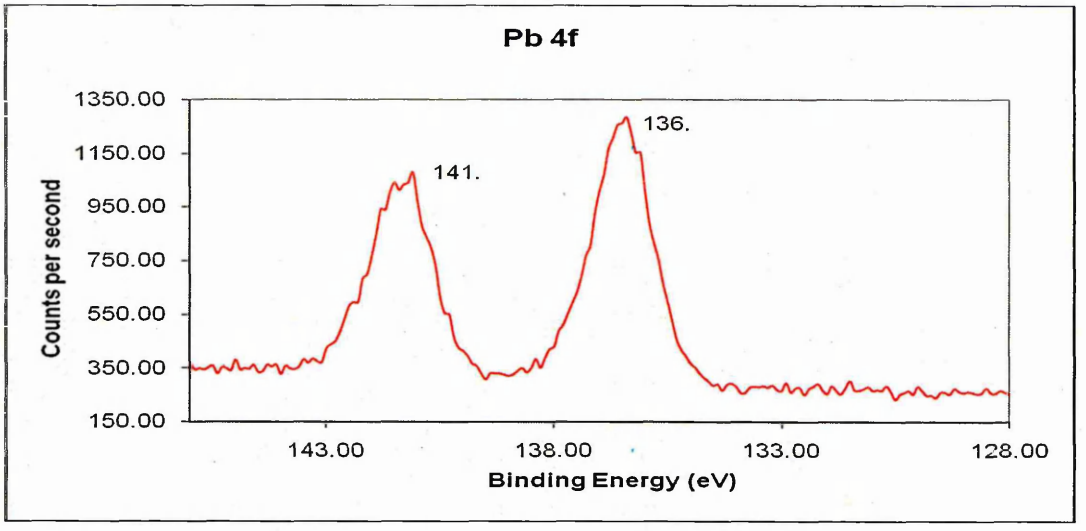

Figure 5.17 Detailed XPS analysis of the spectrum for lead contaminated soil, over the region of the lead 4f spectral line

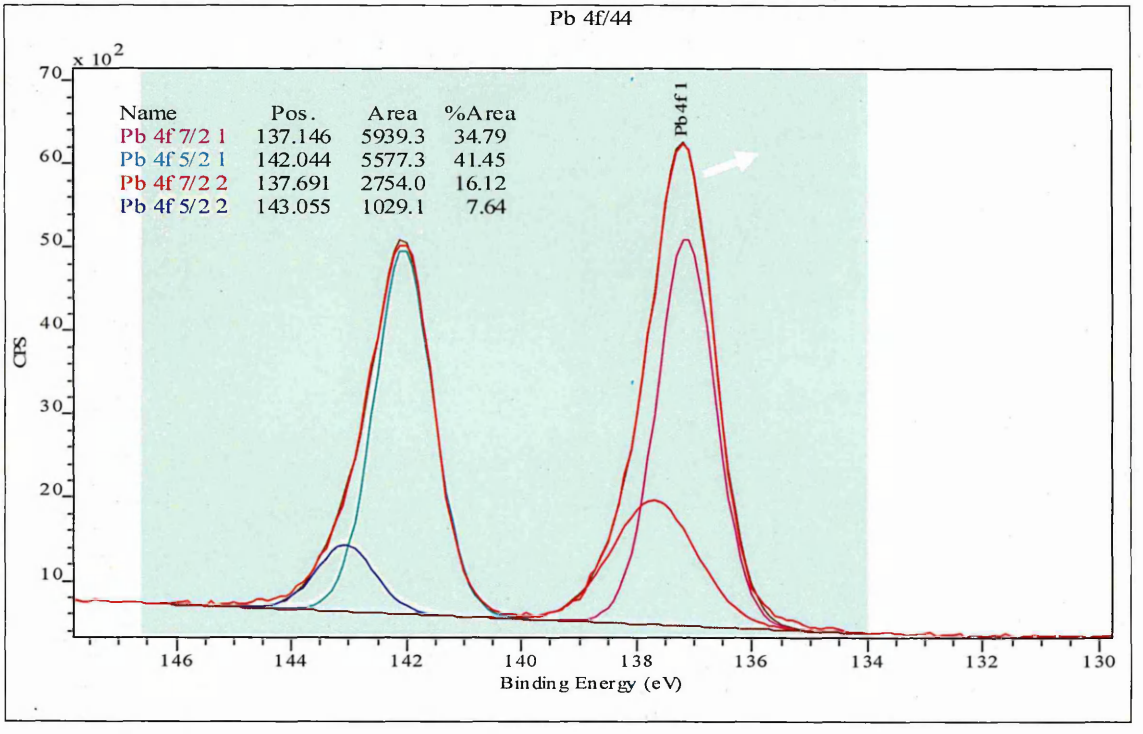

Figure 5.18 Distribution of lead peaks on wide scan by XPS for Pb4f/44

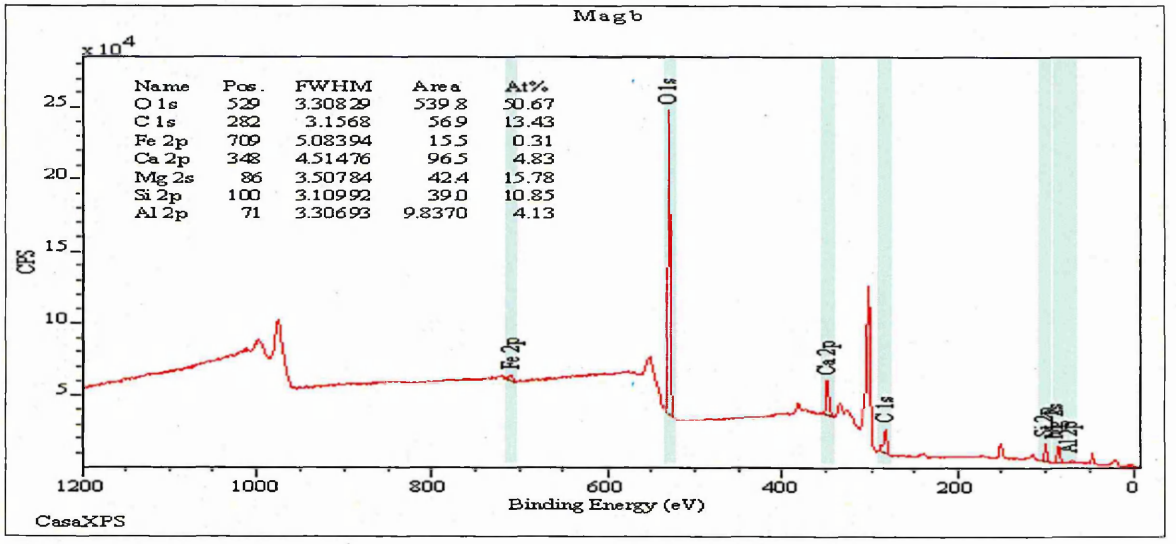

Figure 5. 19 XPS wide scan of magnesia stabilized uncontaminated soil

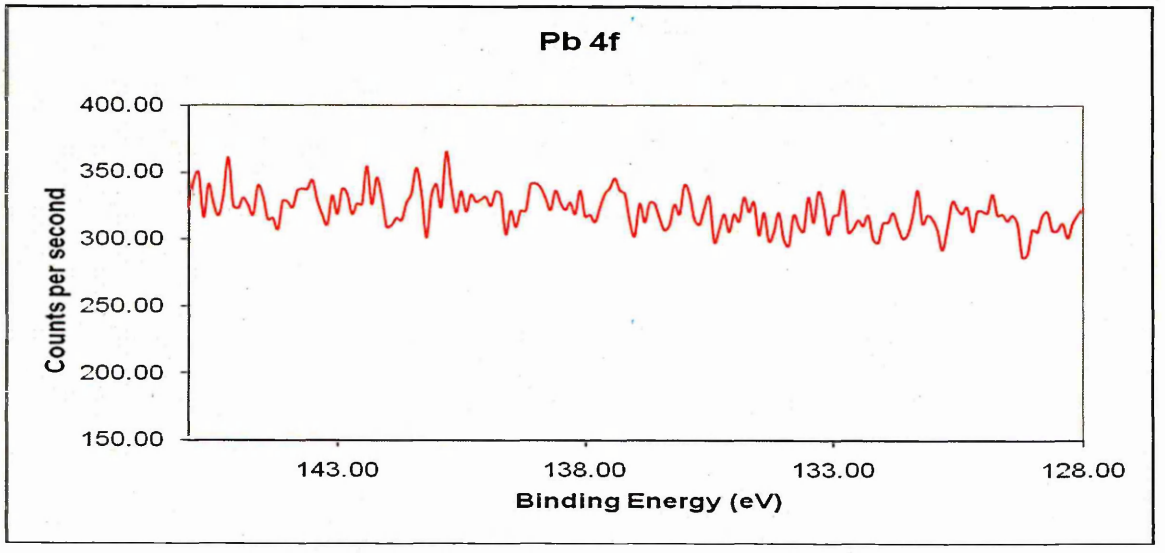

Figure 5.20 Detailed XPS analysis of the spectrum for magnesia stabilized uncontaminated soil, over the region of the lead 4f spectral line

Chapter Six

Effect of GGBFS on metal contaminated soils and solutions

6.1 Background

This chapter reports on the investigation into the possible use of GGBFs for the stabilization of heavy metals in solutions and soils. GGBFS is a heterogeneous compound of oxide materials such as CaO, Fe_2O_3, SiO_2, Al_2O_3 and MgO, the relative proportions of which vary slightly depending on the raw materials and processes used. This variation must be borne in mind because it may affect the use of GGBFS for the removal of heavy metal from aqueous solutions and soils [Xue et al 2009].

The metal leaching behaviour of synthetically prepared contaminated soil containing 780 µg/g lead was investigated after the addition of GGBFS in an attempt to stabilise the contaminant. The leaching behaviour of lead was investigated using 5 grams of soil thoroughly mixed with 0.1g of the stabilising material in a polypropylene container to which 50ml of either deionised water, 0.01M HNO_3 or 0.1M HNO_3 was added.

6.2 The effect of GGBFS on contaminated soil and contaminated solution

The chemical composition of GGBFS is CaO 40–60%, SiO_2 25–35%, Al_2O_3 10–15%, Fe_2O_3 3–9%, FeO_7 and MgO 3–13% [Xue et al, 2009; Sisomphon, 2009]. The presence of C3S (Tricalcium, $Ca_3Al_2O_4$), C2S (Dicalcium silicate (belite) Ca_2SiO_4, C4AF (Tetracalcium aluminoferrite, $Ca_4Al_nFe_{2-n}O_7$) and C2F endorses the cementitious properties of GGBFS but because the C3S content in the steel slag is much lower than in OPC, steel slag should be regarded as a weak Portland cement clinker [Tsakiridis et al 2008]. Also the presence of free MgO is extremely important with regard to the volume stability of GGBFS. [Geiseler 1996]. The composition of the GGBFS used in this project was analysed by XRF and the results are shown in Table 6.1. The results are well within the accepted variations found in GGBFS. It can be seen that the content of the GGBFS used was mainly CaO (39.1%) and SiO_2 (35.6%). Also present are oxides such as Al_2O_3, MgO and Fe_2O_3. The relative proportions of these oxides change when GGBFS from different sources is used. Prior to using GGBFS in the remediation process, the pH value of the GGBFS in deionised water was found 10.2, Sang et al [2009] reports are in agreement with this results , (see Table 6.1). GGBFS is the main component of alkali-activated, cementitious slag materials. Calcium silicate hydrates with a low Ca/Si ratio, hydrotalcite-type phase, some amounts of hydrogarnets and sodium zeolites form as the main alkali-activated cementitious slag hydration products. The microstructures of alkali-activated slag pastes show a higher degree of gel pore content relative to OPC pastes.

Table 6.1 Chemical composition (by mass%) for GGBFS and soil used in this study

Compound in (%)	pH	CaO	SiO_2	Al_2O_3	MgO	SO_3	Fe_2O_3	Mn_3O_4	K_2O	Na_2O	TiO_2
GGBFS	10.2	39.1	35.62	13.13	8.35	4.18	0.77	0.77	0.4	0.3	0.21
Soil	6.9	0.12	93.62	2.89	0.13	0.06	0.65	0.01	1.72	0.21	0.08

pH measured for 0.1g of GGBFS or soil in 50ml DI water

The microstructure and phase composition of the hydrated slags indicate that they can play an important role in immobilising heavy metals in terms of removing the metal by adsorption and precipitation with increase in pH [Deja 2002]. The hydration of GGBFS initially proceeds much slower than OPC, but the products of hydration are similar in terms of chemical make-up, i.e. calcium-silicate hydrates. This hydration of the GGBFS depends on the activation of the glassy structure by the hydroxyl and soluble alkali ions available from the OPC hydration [Hogan et al 2001]. From previous experiments in this study carried out to investigate the primary stabilizer materials (OPC and lime), optimum conditions for operation of the batch leaching test were determined for a lead contaminated solution. The same conditions were used to investigate the effect of GGBFS on soils contaminated with lead.

Table 6.2 shows the results obtained from the leaching of lead contaminated soils with a leaching fluid of 50 ml of deionised water, 5 g of contaminated soil and 0.1g of GGBFS powder, which was 2% of the mass of the soil the ratio of S/L was 1:10. The sample was placed on the platform shaker for two hours before the final leaching solution was filtered using 542 Whatman paper and the concentration measured by ICP. The leachability of lead was determined by the digestion test. For more details of the contamination procedure see Chapter 2, Material and Methods. Table 6.3 shows the effect of GGBFS on the concentration of lead leached from the contaminated soils using 50ml of de-ionised water, and also the release of compounds of Cl^-, NO_3^-, and SO_4^{2-} into the leaching fluid. As shown in Tables 6.2 and 6.3, the amount of lead in the leachant was reduced to undetectable levels as a result of mixing the contaminated soil with GGBFS. The effect was obviously due to the increase in the pH level from 5.4 to 7.4, with a consequent increase in the amount of Ca, Mg, Al and K in the leachant, compared to untreated soil. These results are in agreement with Deja [2002], who used concentrations of GGBFS of 1% and 2% in the contaminated soil, and Dimitrova [1996] who used 1g of GGBFS to remove metals of 1000 mg/l concentration under conditions of controlled pH, and reported that adsorption of metal ions by blast-furnace slag occurs mainly by an ion exchange mechanism. The process is accompanied by partial

dissolution and subsequent hydrolysis of calcium silicates and alumino-silicates of the slag. The possibility of ion exchange occurred by replacement of calcium ion (for chemical equations describing the process see section 6.2.5 in this chapter).

Chaa et al [2006] have used GGBFS as a low-cost adsorbent in water and wastewater treatments, replacing granular activated carbon. Xue et al [2009] used 13.4 g/l of GGBFS as an adsorptive in single and multi-systems of metal solutions, including lead. Similarly, Jin Jiam, et al [2006] have reached 95% of removal of Ni from a contaminated system also Ososkov et al [1993] used 75:1, solvent /slag, and achieved 95% reduction of the leaching of Cr from soils.

Sang et al [2009] used 2-5% of steel slag furnace to amended metals contaminated soils and reported 98 % reduction of lead, zinc and Cd. The pH were increase from 5.7 to 6.2

Chen et al [2000] reported that steel furnace the most effective as amendment on reducing the Cd concentration .Allan et al [1995] have used GGBFs to remediated the Cr III and Cr VI in soil and reported increased of reduction of Cr form 1000 mg./l to 5 mg/l as result of increased adding GGBFs to about 80 % of total samples that stabilized material to contaminated soil were 1 :5 , while in this study 1:100 ratio were used which is 0.1g to 5 g of contaminated soil in this study the chromium were as salt nitrate CrIII.

As in previously chapters an acid wash (0.001MHNO_3) was used on the filter and glassware after conducting the leaching tests. The concentration of lead in the wash solution increased, which demonstrates that lead was precipitated, and remained, on the surface of the filter and the glassware. However the amount of precipitation on the surface of funnel and filter showed that more lead was bound by GGBFS than either lime or OPC, using 0.1M HNO3 as leaching fluid for OPC it was 579µg/g, lime was 711µg/g but GGBFS none. (See table 6.4, see Table 3.6 and 4.9). Laforest and Duchesne [2005] reported similar findings with better stabilization of Cr by GGBFS than OPC at low concentrations. Duchesne and Laforest [2004] produced similar results.

Table 6.2 Effect of GGBFS on concentration of lead(μg/g) and other elements leached from artificial lead contaminated soils by 1000mg/l of lead solution(n=3)

Sample	Pb (μg/g)	Mg (μg/g)	Al (μg/g)	Ca (μg/g)	Na (μg/g)	K (μg/g)	pH of leachant
5g contaminated soil leached with 50 ml of DI water	34.0	22.3	ND	141	ND	13	5.0
5g contaminated soil leached with 50 ml of DI water	33.5	17.1	ND	137	ND	17	5.5
5g contaminated soil leached with 50 ml of DI water	39.0	15.3	ND	130	ND	23	5.7
Mean	39.1	19.3	ND	143	ND	17.5	5.4
Sd	0.77	3.0	ND	5.7	ND	4.1	0.31
Acid wash of filter and glassware for contaminated soil	610.2	NM		NM	N/N	NM	NM
Acid wash of filter and glassware for contaminated soil	580.3	NM		NM	NM	NM	NM
Acid wash of filter and glassware for contaminated soil	585.4	NM		NM	NM	NM	NM
Acid wash of filter and glassware for contaminated soil	604.6	NM		NM	NM	NM	NM
Mean	595.1						
Sd							
5g Contaminated soil + 0.1g of GGBFS leached with 50 ml of DI water	ND	14.4	ND	175.2	0.11	13	7.5
5g Contaminated soil + 0.1g of GGBFS leached with 50 ml of DI water	ND	14.9	ND	181.2	ND	26	7.6
5g Contaminated soil + 0.1g of GGBFS leached with 50 ml of DI water	ND	16.9	0.14	179.6	ND	18	7.2
Mean	ND	15.4		179		19	7.4
Sd	ND	1.3		3.1		6.2	0.16
Acid wash of filter and glassware for 5g contaminated soil + 0.1g of GGBFs	300	NM	NM	NM	NM	NM	NM
Acid wash of filter and glassware for 5g contaminated soil + 0.1g of GGBFs	412	NM	NM	NM	NM	NM	NM
Acid wash of filter and glassware for 5g contaminated soil + 0.1g of GGBFs	420	NM	NM	NM	NM	NM	NM
M	377.3						

N/D=negative value, NM: not - measured

Table 6.3 Effect of 0.1g of GGGBFS on lead contaminated soil by 1000mg/l of lead Solution

Sample	Conc. of Pb (µg/g)	Mg (µg/g)	Al (µg/g)	Ca (µg/g)	Na (µg/g)	K uµ/g)	pH	Cl^- (µg/g)	NO_3^- (µg/g)	SO_4^{2-} (µg/g)
5g contaminated soil leached with 50 ml of DI water	34.0	22.3	0.95	140.7	ND	13	5.0	16.7	613	15.3
5g contaminated soil leached with 50 ml of DI water	33.5	17.1	ND	136.8	ND	17.2	5.5	5.5	582	22.1
5g contaminated soil leached with 50 ml of DI water	39.0	15.3	ND	129.9	ND	23	5.7	9.3	865	24.7
Mean	39.1	19.3		143.0		17.5	5.4	9.4	731	26.0
Sd	7.7					4.1				
5g Contaminated soil + 0.1g of GGBFS leached with 50 ml of DI water	ND	171	ND	1368	ND	172	7.5	6.68	620.2	25.4
5g Contaminated soil + 0.1g of GGBFS leached with 50 ml of DI water	ND	153	ND	1299	ND	230	7.6	13.43	689.4	23.6
5g Contaminated soil + 0.1g of GGBFS leached with 50 ml of DI water	ND	225	1.4	1645	1.3	168	7.2	9.63	688.4	34.1
Mean		183		1437		190	7.4	9.91	666.0	27.7
Sd						6.2				
5g uncontaminated soil leached with 50 ml of DI water	ND	ND	ND	ND	ND	ND	6.9	5.15	128.3	7.7
5g uncontaminated soil leached with 50 ml of DI water	ND	ND	ND	ND	ND	ND	6.9	6.0	131.7	11.3
5g uncontaminated soil leached with 50 ml of DI water	ND	ND	ND	ND	ND	ND	6.9	5.5	121.2	9.6
Mean	ND	ND	ND	ND	ND	ND		5.5	127.1	9.6
Sd	ND	ND	ND	ND	ND	ND		0.4	5.3	1.7

ND=not detected

The change of the pH from 5.4 to 7.5 resulted in the removal of Pb from soils being reduced from 39.3μg/g to an undetectable level. The increase in pH level increased Ca release from 143.0 to 1437μg/g. It also increased the release of Mg from 19.3 to 183μg/g, and K from 17.5 to 190μg/g, see Table 6.2. Chaa et al [2006] claims to have observed an increase in the release of SO_4^{2-} as a result of adding GGBFS, but no significant change was observed in these experiments, nor was any significant change observed in the amount of Cl^- and NO_3^- released. However, the presence of lead in the soil increase the release of SO_4^{2-}, Cl^-, and NO_3^-, compared to uncontaminated soil. The addition of GGBFS to the contaminated soil appeared to make no difference to the release of SO_4^{2-}, Cl^-, and NO_3^-, see Table 6.3. Similar Arya and Xu [1995] reported that chloride binding capacity of GGBFS which resulted in a lowering of the Cl^- concentration in the pore solution

The GGBFS hydration products are generally found to be more gel-like, as compared to cement, and tend to fill voids contributing denseness to the cement paste. It is this property that is responsible for the increased ultimate strength and the enhanced durability in terms of sulphate resistance, penetration of chlorides, and alkali-silica reactivity [Hogan et al 2001].

In support of this result, Ahn et al., [2003] applied GGBFS to remediate the arsenic in a contaminated system and suggested that as may also be removed by adsorption onto iron oxides if the pH is lowered to near-neutral 5-7. However, in this study the pH level increased from 5.4 to 7.4 as a result of adding GGBFS but not only the pH factor affected the lead behaviour it is also the adsorption capacity of GGBFS, (see Table 6.2). Rha et al .[2000] reported Gypsum induced the structural densification of slag through the formation of AFt (Alumina,Ferric-oxide, tri-sulphate(ettringite) and AFm(alumina, ferric oxide, monosulfate) phase. Therefore, the lead ion leaching amount decreased. However, the term ettringite has come to be used in a generic sense to represent the AFt phases formed as a result of C3A or C4AF hydration with gypsum in water.[Henderson 1995] (see Table 3.3) for definition .

6.2.2 Effect of Variation of pH in the Leaching Fluid

The choice of the extracting reagent depends on the metal type, metal concentration, metal fractionation/speciation, and soil characteristics. Strong acids such as (HCl) or (HNO_3) and chelating agents such as Ethylenediaminetetra-acetic acid (EDTA) are commonly used to extract heavy metals from soils [Dermont et al 2008]. In this study leaching fluids with a range of pH levels were tested which is the nitric acid.

Table 6.4 Effect of GGBFS on release of Pb, Ca, Mg, Na and K with variation in pH with HNO_3 as leaching fluid

Leaching fluid	Sample	pH of leachant	Conc. of Pb in leachant (µg/g)	Sd	Conc. of Ca in leachant (µg/g)	Conc of Mg in leachant (µg/g)	Conc. of Na in leachant (µg/g)	Conc. of K in leachant (µg/g)
D.I. water	5g contaminated soil	5.4	37.6	**3.1**	**143**	19.3	**5.4**	17.5
	0.1g GGBFS + 5g contaminated soil	7.4	ND		1437	183	1.1	190
0.01MHNO$_3$	5g contaminated soil	2.2	744	23	2400	270	4	19.6
	0.1g GGBFS + 5g contaminated soil	6.3	7.03	0	8500	710	12	36
0.1MHNO$_3$	5g contaminated soil	1.2	858	38	2600	280	5	22.1
	0.1g GGBFS + 5g contaminated soil	1.2	ND		30533	2560	41.9	96

ND=not detected

Previous tests, reported in Chapter 3, Table 3.6, have shown that the release of lead from untreated, uncontaminated soil was 37.6µg/g using DI water pH 5.6, while with 0.01HNO_3 pH 2.1 the result was 744µg/g, and using 0.1M HNO_3 solution at pH 1.1 the result was 858µg/g. The effect of pH of the leachant fluid on the amount of lead removed has also been reported by Jing et al [2004] who examined the 'Toxicity Characteristic Leaching Procedure test' using an extraction fluid with pH 5.1 and DI water with pH 7.7. The Pb extracted was reduced from 5.9mg/l for untreated soil to less than 0.7mg/l.

The effect of adding GGBFS to the contaminated soil was investigated using HNO_3 as leaching fluid with different pH values, see Table 6.4. The pH value are average of many experimental were conducted (n=3) . GGBFS was found to be effective at stabilizing the lead in the soil. The addition of GGBFS to contaminated soil when the leachant was DI water has been described above. With the addition of GGBFS, the pH of the leachant with the 0.01M HNO_3 solution rose from 2.2 to 6.3, and the concentration of lead fell hundredfold, from 744 to 7µg/g. The results are the average value of three samples. With 0.1MHNO_3 the initial pH value of the leachant was 1.2, and with the addition of the GGBFS remained at 1.2. The concentration of lead in the leachant fell from 854µg/g to non detectable level. With the addition of GGBFS. The conclusion from this study is that the addition of GGBGS increased the pH level of the leachant and decreased the level of lead in the leachant. With contaminated soil alone, the largest release of Ca, Mg, Na and K was obtained using a

leaching fluid with pH 1.2. The addition of GGBFS increased the pH value of the leachant and the release of Ca, Mg, Na and K. The maximum release occurred with the lowest pH, see Table 6.4. Albion et al [1996] have reported results which are in agreement with those presented here using acid with a pH value of below 4. Ososkov et al [1993] have reported that at low pH (1.5) and high concentration of sulphuric acid the leaching fluid achieved a greater reduction of Cr leached from soils by about 95 %.

The results of the leaching test presented in Tables 6.3 show high contents of Ca, K and Na in the GGBFS leachate. It is well known that high calcium hydroxide and calcium silicate levels occur in the leachate (Ahn et al., 2003; Dimitrova and Mehanjiev, [2000]; Yan et al [2000], but here it was noticeable that the leachate also contained high potassium levels even though the potassium content of the GGBFS was at lower proportional , see Table 6.1. Leaching of other metal ions was not significant, probably due to the adsorption of metal ions on the surface of GGBFS at high pH levels. Chaa et al [2006] and Negim.O, et al [2009] have reported that a proportion of the added GGBFS is effective in decreasing the concentration of Cu in soil, and that increasing the proportion of GGBFS from 2% to 4% increased the pH level to 9 in the final solution.

The strength of the contaminating solution was increased to 20,000 mg/l, and the results in Table 6.5 show that GGBFS was still effective as a stabilizer and reduced the release of Pb into the leachant to very low levels (0.6 mg/l). The addition of GGBFS to the contaminated soil also reduced the proportion of NO_3^- in the DI water leachant from 731µg/g to 666µg/g. However, for Cl^- there was no statistically significant change in the proportion removed in the leachant only10 µg/g, and for SO_4^{2-} there appeared to be a slight increase in the proportion in the leachant 116.7 µg/g and with no added GGBFS 42µg/g. (See Table 6.3). In presence of the contaminant there was a high release of anions compared with uncontaminated soils.

Table 6.5 Effect of addition of GGBFS to soil contaminated with lead at 20,000mg/l(n=3)

Sample	Conc. of Pb in leachant (µg/g)	Conc. of Cl^- in leachant (µg/g)	Conc. of NO_3^- in leachant (µg/g)	Conc. of SO_4^{2-} in leachant (µg/g)	pH
1000ml of 20 000 mg/l solution + 5g contaminated soil, leached with 50 ml of DI water	3689	9.4	5750	45	5.0
1000 ml of 20 000 mg/l solution + 5g contaminated soil, leached with 50 ml of DI water	3630	11.5	5600	50	5.5
1000ml of 20 000 mg/l solution + 5g contaminated soil, leached with 50 ml of DI water	3710	13.0	5800	59	5.7
Mean	3676	11.3	5717	51	5.4
Sd	41				0.38
1000 ml of 20 000 mg/l solution + 5g contaminated soil + 0.1g of GGBFS leached with 50 ml of DI water	ND	16.4	4677	124.6	7.5
1000 ml of 20 000 mg/l solution + 5g contaminated soil + 0.1 g of GGBFS leached with 50 ml of DI water	ND	17.0	4500	116	7.6
1000 ml of 20 000 mg/l solution + 5g contaminated soil + 0.1 g of GGBFS leached with 50 ml of DI water	ND	15.0	4700	109.5	7.2
Mean	ND	16.1	4626	116.7	7.4
Sd					0.16
5g uncontaminated soil leached with 50 ml of DI water	ND	5.2	128	7.7	6.8
5g uncontaminated soil leached with 50 ml of DI water	ND	6.0	132	11.3	6.7
5g uncontaminated soil leached with 50 ml of DI water	ND	5.5	121	9.6	6.9
Mean		5.5	127	9.6	6.9
Sd		0.4	5.3	1.7	

6.2.3 The effect of GGBFS on soil contaminated with Pb, Cd, Cr, Cu, Ni and Zn

The effect of the addition of GGBFS to a soil sample contaminated with a mixture of heavy metals was investigated using the same procedure as for testing its effect on soil contaminated with lead alone. The procedure for contaminating the soil with the mixture of metals has been described in Chapter 3, Section 3.4.2. The solution used to contaminate the soil contained a 1000mg/l mixture of the heavy metals Pb, Zn, Ni, Cd, Cr, and Cu in DI water. The leaching batch tests were conducted for 2 hours on the platform shaker. The S/L ratio was 1:10 and the leaching fluid was 50ml of deionised water.

When the soil was treated with 0.1 g of GGBFS, there was substantial reduction in the concentrations in the leachant of each of the six metals contaminating the soil(see Table 6.6). For Pb, Zn, Ni and Cr the reduction was greater than 95%. For Cd and Cu the reduction was 92%. The pH in the final leaching fluid was 5.5. The difference in Cl^- levels were not statistically significant while the amount of SO_4^{2-} in the leachant actually increased to 41.2 µg/g.

Albion et al [1996] used GGBFS to reduce the leaching rate of a solution of (Cr. Cd, Pb, Ni, and Zn) prepared from nitrate salts, and reported a large reduction in the leaching rate of metals using calcium silicate hydrate and calcium tri-sulphoaluminate hydrate formation on a matrix of slag. Also Allan et al [1995] used a mixture of 40% GGBFS and 60% OPC to treat Cr contaminated soil and reported a 100% reduction in the Cr leaching rate. Taylor et al [2006] indicated that slag may be suitable for treatment of landfill leachate, domestic, industrial and agricultural wastewater and acid mine drainage, as well as treatment of storm water.

6.2.4 The digestion test for mixture of metals contaminated soils

The maximum extractions of Pb, Cd, Cr, Cu, Ni and Zn obtained for 1g of contaminated soil using the total digestion acid test with 5ml of HNO_3 and 25ml of DI water on a hotplate for 10 min, and filtered with Whatman 543 ashless filters are shown in Table 6.7 and in chapter three Figure 3.4.

Table 6.6 Effect of GGBFS on 5g of soil contaminated with 1000ml of solution containing 1000mg/l of Pb, Cd, Cr, Cu, Ni and Zn, leached with 50ml DI water

Sample	Conc. of Pb in leachant (µg/g)	Zn (µg/g)	Ni (µg/g)	Cd (µg/g)	Cr (µg/g)	Cu (µg/g)	pH	Cl^- (µg/g)	NO_3^- (µg/g)	SO_4^{2-} (µg/g)
Metal contaminated soil + DI water	857	880	905	987	881	927	4.0	17.1	18890	20.7
Metal contaminated soil + DI water	883	1065	1084	1193	902	1107	4.0	17	18751	33.7
Metal contaminated soil + DI water	912	946	975	1056	933	980	3.9	11.2	16370	30.0
Mean	884	964	988	1079	905	1005	4.0	15.1	18003.2	28.1
Sd	27.7	93.7	90.2	104.9	26.2	92.5		3.3	10208	6.7
Metal Contaminated soil + GGBFS	6.43	16.9	18.67	66.63	6.74	56.3	5.4	13.6	16558	47.2
Metal Contaminated soil + GGBFS	7.52	19.6	21.09	50.4	7.79	43.3	5.9	7.72	6999	29.3
Metal contaminated soil + GGBFS	44.49	60.75	67.97	128	45.7	122.9	5.4	14.4	16558	47.2
Mean	19.48	32.41	35.91	81.67	20.07	74.2	5.6	11.9	13372	41.2
Sd	21.6	24.5	27.7	40.92	22.19	42.7		3.6	5519	10.2
uncontaminated soil	ND	ND	ND	ND	ND	ND	6.3	5.2	128.3	7.7
uncontaminated soil	ND	ND	ND	ND	ND	ND	6.7	6.0	131.7	11.3
uncontaminated soil	ND	ND	ND	ND	ND	ND	6.8	5.5	121.2	9.6
Mean	ND	ND	ND	ND	ND	ND	6.6	5.5	127.1	9.5
Sd								0.4	5.3	1.7

6.2.5 Effect of GGBFS on a solution contaminated with lead

The effect of adding 0.1g of GGBFS to each of three separate solutions containing lead concentration levels of 50, 100 and 1000mg/l was investigated. The lead solution was thoroughly mixed with 0.1g of GGBFS to allow the investigation of the presence of lead compounds in the GGBFS. The findings reported below are in agreement with Ortiz et al, [2001] who used 1g of GGBFS to achieve an 85% reduction of Ni in the leachant at a pH of between 5 and 6.

When the GGBFS comes into contact with water, some of the components, particularly free lime (CaO), may dissolve partially into solution [Shen and Forssberg 2003] which causes an increase at pH in the final solution, see Tables 6.7, 6.8 and 6.9. The levels of NO_3^- shown in Table 6.9 were the highest obtained, because the lead was added as lead nitrate, $Pb(NO_3)_2$. The volume of each solution was 50 ml.

There appears to be no significant difference in the release of Ca, K and Mg for lead concentrations between 50 and 100mg/l. However, when the lead in solution was increased to 1000mg/l there was a significant increase in the concentrations of Ca, K and Mg in the leachant. As a result of adding GGBFS to the solution there was an increase in the pH level of the leachant due to the high content of CaO, Si, AlO_3 and MgO in the slag. During the hydration process in the presence of water, the amount of slag is important only in acidic solution, which has pH > 6, as also observed by Dimitrova and Mehendgive [1998].

The precipitation, adsorption and redox reactions that immobilize contaminants are all strongly influenced by pH [Batchelor 2006]. At high pH levels above 8.5 .Yan et.al.[2000], reported that the surface of the GGBFS is negatively charged and adsorbs cations, such as sodium and metal ions [Ortiz et al,2001; Ramakrishina and Viraraghavan1997]. Dissolution of slag and adsorbed metal ions occurs at either low pH about 2 or high temperature. [Ortiz. et al 2001]. With changing pH levels, the properties of GGBFS may change and the release of toxic elements may occur during the leaching process [Chaa et al 2006]; Nilforoushan and Otroj, 2008]. Dimitrova and Mehendgive[1998] reported 97% removal of Pb ion from solution at pH rang 6-7, which is in agreement with the results obtained in this study that achieved 100% removal of Pb ion from solution and the pH in the final solution was 7-7.3 (see Table 6.8 and 6.7). Sheng .et al, [2010] used 3g of steel slag to stabilize 500mg/l of 100 mg/l Pb and reported 100% reduction of concentration and removal of lead from solution. Kang et al [2005] used only 1 g of steel slag to stabilize 200ppm of Pb solution, these results suggest that the wastes from the steel making processes could be used as an efficient adsorbent for the removal of heavy metals in wastewater. This is in a similar trend with this study which concluded that steel slag works as an adsorbent of Ionic lead.

Table 6.7 Effect on pH level of 0.1g of GGBFS in 50ml of lead solution of strength 50mg/l

Sample	Conc. of Pb (mg/l)	pH of final solution	Mg (mg/l)	Ca (mg/l)	Na (mg/l)	K (mg/l)
0.1g GGBFS + 50 mg/l of Pb solution	ND	7.2	2.14	62.2	0.58	0.19
0.1g GGBFS + 50 mg/l of Pb solution	ND	7.0	2.68	70.5	0.45	1.45
0.1g GGBFS + 50 mg/l of Pb solution	ND	7.4	3.83	81.5	0.37	0.49
M		7.2	2.88	71.4	0.47	0.71
Sd		0.18	0.86	9.7	0.14	0.65
50 mg/l of Pb solution	49	4.0	ND	ND	ND	ND
50mg/l of Pb solution	50	3.9	ND	ND	ND	ND
50 mg/l of Pb solution	51	4.0	ND	ND	ND	ND
Mean	50	4				
Sd						
acid wash (filter and funnel)						
0.1g GGBFS + 50mg/l of Pb solution	29	NM	NM	NM	NM	NM
0.1g GGBFS + 50mg/l of Pb solution	35	NM	NM	NM	NM	NM
0.1g GGBFS + 50mg/l of Pb solution	37	NM	NM	NM	NM	NM
Mean	36.7					
Sd						

ND=none detected , NM=not measured

Table 6.8 Effect on pH level of 0.1g of GGBFS in 50ml of lead solution of strength 100mg/l

Sample	Conc of Pb (mg/l)	pH of final solution	Mg (mg/l)	Ca (mg/l)	Na (mg/l)	K (mg/l)
0.1g of GGBFS + 100 mg/l of Pb solution	ND	7.0	2.77	71.2	0.32	0.22
0.1g of GGBFS + 100 mg/l of Pb solution	ND	7.3	1.62	56.6	0.33	0.39
0.1g of GGBFS + 100 mg/l of Pb solution	ND	7.6	1.9	65.0	0.34	0.42
Mean		7.3	2.0	64.26	0.3	0.3
Sd		0.33	0.59	7.31	0.01	0.10
100 mg/l of Pb solution	99.0	3.3	ND	ND	ND	ND
100 mg/l of Pb solution	98.6	3.3	ND	ND	ND	ND
100 mg/l of Pb solution	99.0	3.4	ND	ND	ND	ND
M	98.9	3.3	ND	ND	ND	ND
Sd	0.01					

ND=non detect

Table 6.9 Effect of 0.1g of GGBFS in 50ml of lead solution of strength 1000 mg/l. Quantities of anions of Cl, NO_3, and SO_4 released as a consequence of leaching fluid of pH 7.5

Sample	Pb (mg/l)	Mg (mg/l)	Ca (mg/l)	Na (mg/l)	K (mg/l)	Cl^- (mg/l)	NO_3^- (mg/l)	SO_4^{2-} (mg/l)
0.1 g of GGBFS + 1000 mg/l of Pb solution	0.58	19.76	981	6.75	2.61	1.17	953.9	18.67
0.1g GGBFS + 1000 mg/l of Pb solution	0.78	17.84	872	4.93	2.27	0.85	914.4	14.87
0.1 g of GGBFS + 1000mg/l of Pb solution	0.48	24.16	1018	7.12	2.84	2.04	927.2	21.36
M	0.61	12.61	957	6.27	2.57	1.35	931.8	18.3
Sd	0.152	3.24	75.7	1.17	0.28	0.61	20.15	3.

6.2.5.2 The Effect of GBBFS on a mixture of metals contaminated solution

Table 6.10 Effect of GGBFs on a mixture of five metals in solution, Cu, Pb, Cd, Ni, and Cr, concentration 100mg/l and 50mg of metal solution

sample	Pb (mg/l)	Ni (mg/l)	Cd (mg/l)	Cr (mg/l)	Cu (mg/l)	pH	Cl^- (mg/l)	NO_3^- (mg/l)	SO_4^{2-} (mg/l)
0.1 g of GBBFs +100 Mix solution	76.2	72.11	100	77.4	76.2	3.4	14.6	1549.1	7.1
0.1 g of GBBFs +100 Mix solution	81.1	68.5	103.8	77.1	77.4	3.41	9.4	1560	3.6
0.1g of GBBFs +100 Mix solution	83.3	77.3	104.7	83.3	84	3.33	7.4	1551	4.22
Mean	80.2	72.63	102.83	79.26	79.2		10.46	1553.36	4.97
Sd	3.63	4.423	2.494	3.496	4.2		3.716	5.82	1.86
blank 100 mg/l metal solution	100	100	100	100	100	3.08	ND	ND	ND
blank 100 mg/l metal solution	100	100	100	100	100	3.06	ND	ND	ND
blank 100 metal mg/l solution	100	100	100	100	100	3.05	ND	ND	ND
Mean									
Sd									

ND=none detected

As result of adding the GGBFS to a mixture of metals (Pb, Ni, Cd, Cr and Cu) the reduction of Pb was only 20 % and Ni was 30 %, 15 % for Cr and Cu, while no effect on Cd concentration was seen(Table 6.10). The increase of pH was only 0.4 units. The mechanism of removal can only be explained as adsorption reaction occurred on the surface of GGBFS at low pH. Dimitrova [1996] reported that blast-furnace slag is an effective sorbent for Cu, Zn and Ni ions in a wide range of ions concentration and pH values. López and Pérez [1998] have used 1- 7.5 g of GGBFS and reported high efficiency of blast furnace slag to remove metals from solution and observed that each time the amount of GGBFS was increased the metal was removed totally by adsorption ,this suggests that the metals in particular Pb and Cu, can be effectively mobilized with GGBFS at high concentration of metal solution, with consideration of the conditions of removal such as level of concentration and temperature.

6.3 Characterisation of Precipitated Materials

6.3.1 Fourier Transformation Infrared Spectroscopy (FTIR)

Here FTIR was used to investigate the bond relations between the lead contaminated soil and solution and stabilized material, and to identify the compounds presents in the samples.The samples were prepared as described in Chapter two.2.2.10, and chapter 3 Section.3.5.1.

Figure 6.1 shows the spectrum for lead contaminated soil and contaminated soil treated with GGBFS. The peaks in the two spectra at 1346cm^{-1}, 1882.1cm^{-1} and 3785.5cm^{-1} are identified as due to lead in the soil. According to Barnett's work on OPC [2002], see Table 6.11, the stretching of the O-H bond of $Ca(OH)_2$ has a peak at 3645cm^{-1}. By analogy it is suggested that the cause of the peak in Figure 6.1 between 3785-3800cm^{-1} can be attributed to the stretching of the O-H bond in $PbCa(OH)_2$. In Section 6.3.3 the results for XRD analysis show agreement with these results. According to Hughes and Metven [1995] who investigated the composition of cement, the peak at 1596cm^{-1} in Figure 6.1 can be attributed to $PbCO_3$ only, and the small peaks at 900-1200cm^{-1} are evidence of the presence of SiO_4 and V-Si-O which is in agreement with XRD investigation reported below.

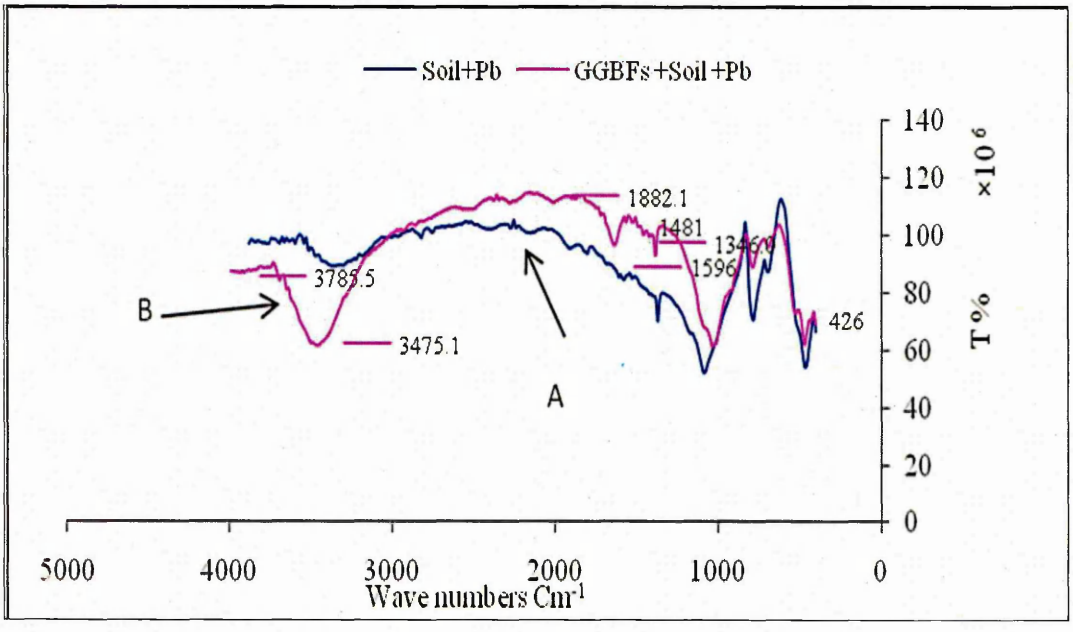

Figure 6.1 FTIR plot for lead contaminated soil and contaminated soil after treatment with GGBFS: (A) Spectrum for lead contaminated soil, and (B) Spectrum for contaminated soil treated with GGBFS

Table 6.11 Principal FTIR frequency bands in hydrated Portland cement (Barnett et al [2002]) compared with this study

Frequencies (cm^{-1})	Assignment	Soil + GGBFS + Pb
3645	stretching O-H of $Ca(OH)_2$	
Zone 3100-3400	symmetric and asymmetric stretching (Vl and V3 of O-H)	3785-3800
1650	Deformation(V2)H_O_H	1608-1882
1480	$V3.CO_3^{2-}$	1481
872	$V2.CO_3^{2-}$	830-1160
712	$V4.CO_3^{2-}$	
970	stretching Si-O(V3) (in polymeric unit of SiO_4^{4-})	
925	stretching Si-O(V3) (in non-hydrated cement)	
522	V4.Si-O	
452	V2.Si-O	426
1115	$V3.SO_4^{2-}$	

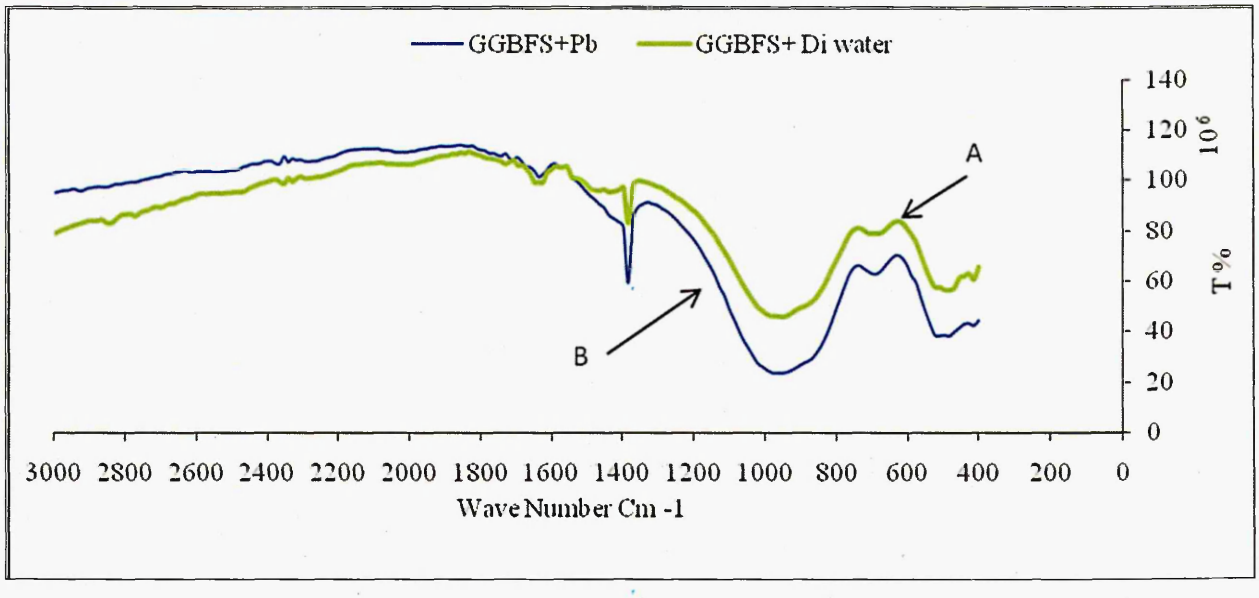

Figure 6.2 FTIR plot of GGBFS and stabilised lead solution, (A) Spectrum for 0.1g GGBFS in 50ml DI water, (B) Spectrum for 0.1g GGBFS in 50ml of lead solution of strength 20 ,000mg/l

6.3.2 RAMAN spectroscopy

Figure 6.3 shows three Raman spectra; one for uncontaminated soil with GGBFS added, the second for soil contaminated with lead solution, and a third for soil contaminated with lead solution and with GGBFS added. Considering the peaks in the Raman spectra, there is a major peak in all three spectra at just under 500cm^{-1}. This is due to deformations of Si-O, tetrahedra(O-Si-O bending) between 430-540cm^{-1}. Kirkpatrick et al [1997] investigated the frequency ranges and assignments for peaks observed in Raman spectra of C-S-H and related these peaks to crystalline hydrous Ca-silicates in general agreement with these results The agreement were on peaks of 462 cm^{-1} where it was reported that internal deformations of Si-O, tetrahedra(O-Si-O bending) occurs between 430-540cm^{-1}.The only clear peak is for lead contaminated soil, around 1040-1100cm^{-1}, which the Raman database attributes to Calcite. According to Guillaume et al [2007] who investigated by Raman mode sulphate, in gypsum and ettringite, this can be assigned to V3$(SO_4)^{-2}$ which shows the formation of lead in soils attributed to $PbSO_4$. This is in agreement with results obtained by FTIR and XRD for lead contaminated soil, see Chapters 3 and 4. It is noted that the Raman technique is not sufficiently powerful to identify the effect of GGBFS on soils as compared with other techniques used in this study e.g. FTIR, XRD and XPS.

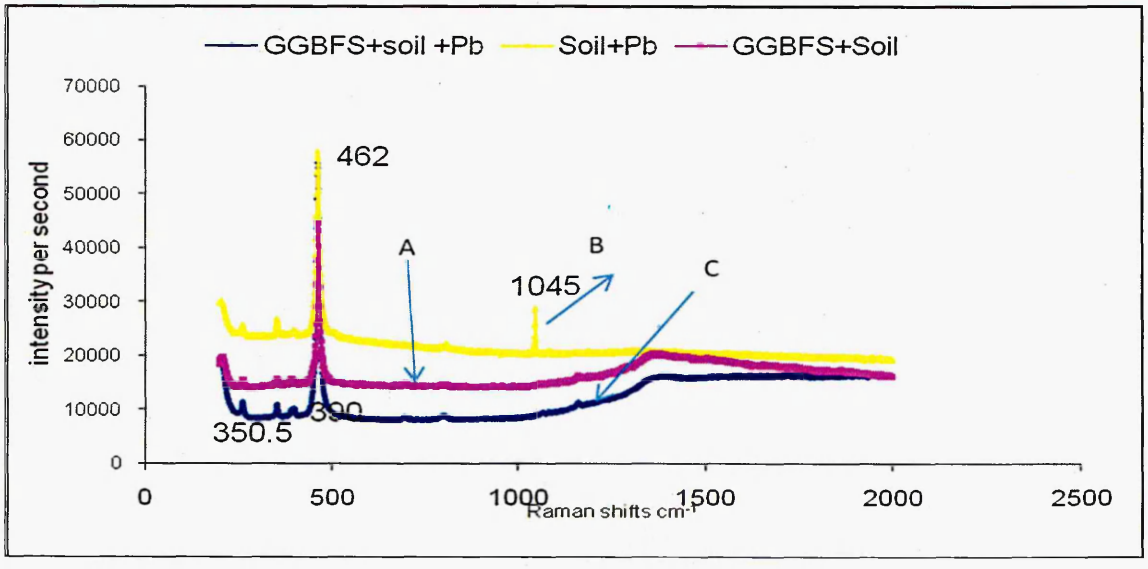

Figure 6.3 Raman spectra for:(A)5g uncontaminated soil + 0.1 g GGBFS, (B) soil of mass 5g contaminated with 50ml of 20,000mg/l of lead solution, (C) as B with 0.1g GGBFS added

Figure 6.4 shows the Raman spectrum for GGBFS in DI water, and for lead contaminated solution treated with GGBFS. No peaks were identified, which clearly distinguished the two

spectra, this is similar to the FTIR results presented in Figure 6.2. The conclusion is that Raman spectroscopy is not an effective technique for this application. Potgieter-Vermaak et al [2006] have reported similarly, that Raman spectrometry of grey cements is routinely not successful and further investigation into the use of different laser methods was advised by these authors.

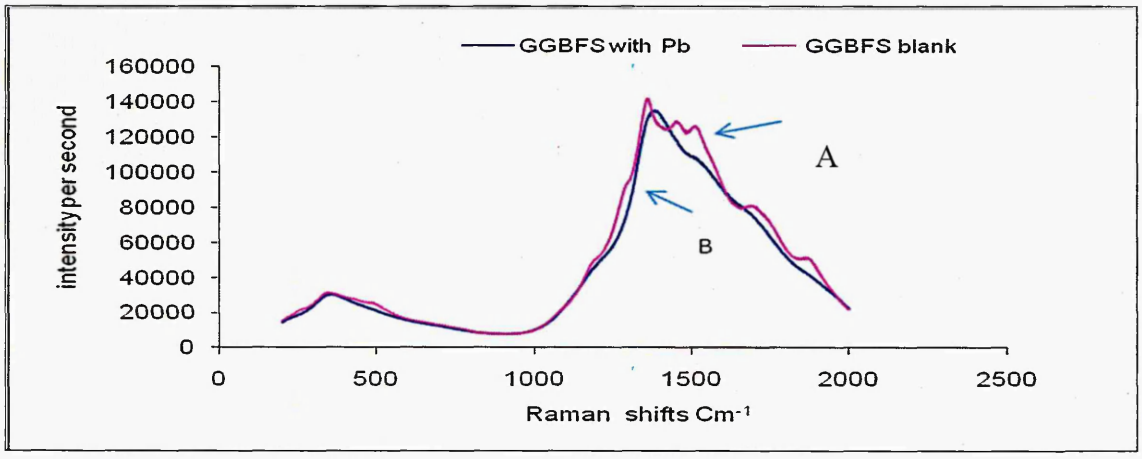

Figure 6.4 Raman spectra: (A) Spectrum for 0.1g GGBFS in 50ml DI water, (B) Spectrum for 0.1g GGBFS in 50ml of lead solution of strength 20 000mg/l

The slag sample was considerably more difficult to analyse due to a large fluorescent background observed with all lasers [Potgieter-Vermaak et al 2006] the GGBFS consisted many minerals, some of which have not been defined, such as calcium silicates, in steel slag some of these minerals have been well characterized with Raman spectroscopy and reported in the technical literature, but no literature could be formed where these have been identified in slag by means of Raman spectrometry. Technical literature regarding the determination of the mineralogical composition by means of Raman spectrometry is limited and it is usually determined by X-ray diffraction (XRD).

6.3.3 X-ray diffraction analysis

The diffraction of X-rays by a sample is dependent on and provides information concerning the atomic structure of particles in a material. This can be particularly useful, for example, when characterising clay minerals according to the separation between layers and/or the ability of these layers to be expanded by the absorption of water. [Crofts 2006]. According to Duchesne and Laforest[2004]. The crystalline part of slag is mainly distributed between the solid solution of the melilite family [from akermanite ($Ca_2MgSi_2O_7$) to gehlenite ($Ca_2Al_2SiO_7$)

composition] and merwinite [$Ca_3Mg(SiO_4)_2$] minerals. The chemical composition of the blast furnace slag shows little variation in a plant and is homogenous from particle to particle.
X-ray diffraction analysis (XRD) was used to investigate a 20 000mg/l Pb solution stabilised by GGBFS. The 20,000mg/l solution was used to enable detection by XRD (and other techniques) to characterize and measure the Pb in the sample. The suggestion from the leaching test analysis using the Inductively Coupled Plasma (AES) technique is that the formation of lead on the surface of the GGBFS is partly by precipitation, as a result of increase in the pH of the final leaching solution, and also by the absorption of lead on the surface of the GGBFS. The latter is confirmed by the Environmental Scanning Electron Microscope (ESEM), see below, which shows the lead on surface of the GGBFS. In addition, the acid wash on the surfaces of the funnel and the ICP measurement proved that lead is being mobilized by GGBFS, see Table 6.2. Rha et al [2000] used ICP, ESEM and XRD techniques to investigate the efficiency with which GGBFs stabilised heavy metals, using similar techniques to those used in this study and reported similar results of efficiency of GGBFS as stabilizer materials.

Figure 6.5 shows the spectra for a solution of 0.1g GGBFS in 50ml DI water and of 50ml of 20,000mg/l lead solution stabilised with 0.1g GGBFS. The scans were from 5-80 theta. According to the International Cambridge XRD database [http://www.cds.dl.ac.uk] the formation of $PbCa_2(Si_30_9)$ and $Pb_4SO_4(CO_3)s(OH)_2$ lead sulphate carbonate hydroxide may be identified by the presence of strong peaks at 29.36° and 29.47° respectively, see Figure 6.5. Although the XRD was run for 2 hours there was significant noise on the spectrum which was due to the glassy content of GGBFS. Pala et al, [2003] reported that the glass content of the slag should be in excess of 90% to show satisfactory properties for using GGBFS.
Rha et al[2000] reported that 2 theta 308°–318° is due to the glass structure CaO–Al O – MgO– 2 3SiO,with a short-range order and observed a peak of type calcium–silicate–hydrates with no crystalline characteristic around 29° which is in agreement with the results reported here .Also [Deja2002] reported that it is possible that heavy metal ions incorporate in to the $CaCO_3$ structure.

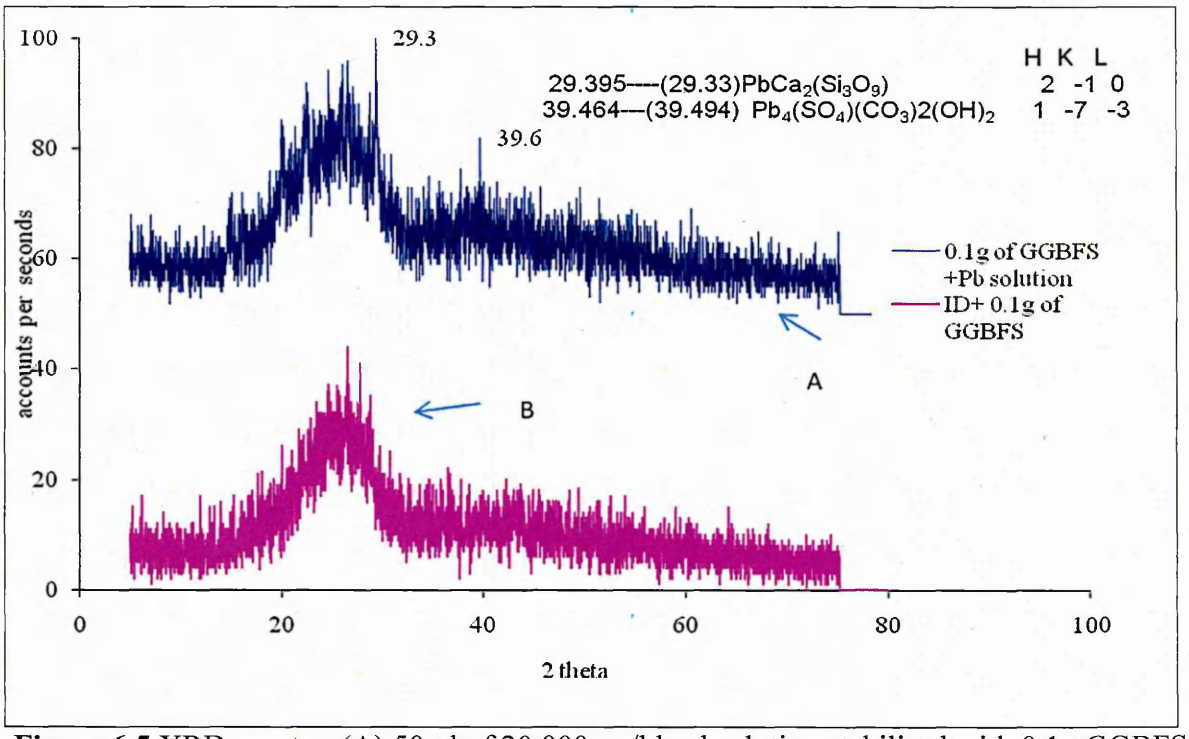

Figure 6.5 XRD spectra, (A) 50ml of 20 000mg/l lead solution stabilised with 0.1g GGBFS, (B)Spectrum for 0.1g GGBFS in 50ml DI water

6.3.4 Environmental scanning electron microscope

Figure 6.6a, shows the precipitation of lead on the surface of slag particles. Energy dispersive X-ray analysis (EDX) of the GGBFS stabilized Pb solution, Figure 6.6b, confirms that lead is present in the sample, but there is no indication of the spherical shape of the lead which can be seen in Figure 6.6a. Taube et al, [2008] have reported the spherical shape of lead in cementitious material, and this is often referred to as lead being adsorbed and incorporated elements such as Ca, Si or Al within GGBFS. The ESEM when used for investigating contaminated soils and contaminated soils treated with GGBFS was operated according to the description given in Chapter 2. Figure 6.7a shows the lead in the treated soils. However, the shape of the lead particles was not quite clear, this was due to its being incorporated within the soil's matrix which had been treated with GGBFS.

In comparison, Figure 3.14 in Chapter 3 shows the lead in the lead contaminated soil to be of spherical shape. This demonstrated that the lead was shaped into the matrix of the soils, which supports the hypothesis of the binding of the lead with GGBFS and soil materials, such as Si, Al and Ca. Other elements shown by EDX to be present are Si and Mg, and high amounts of Fe due to the GGBFS, see Figure 6.7b.

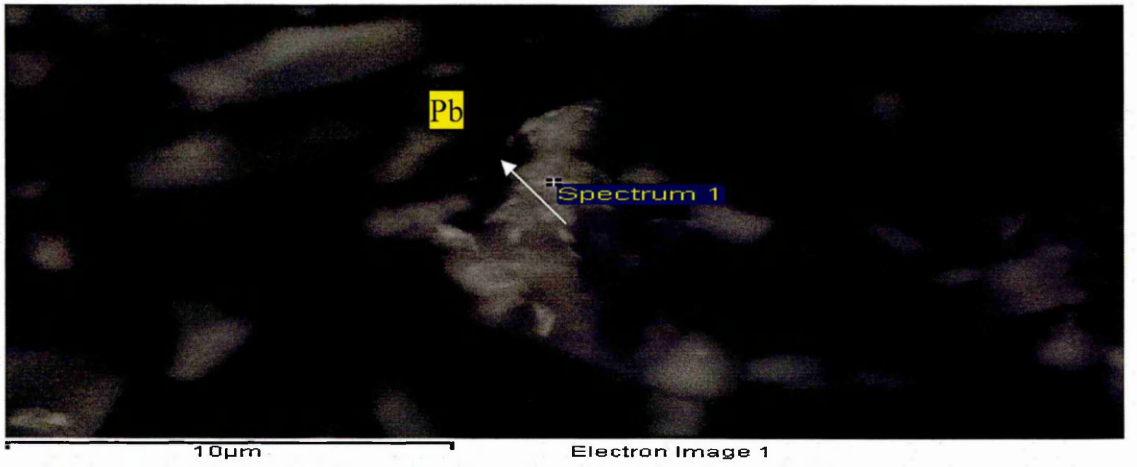

Figure 6.6a ESEM image of GGBFS treated contaminated Pb solution, Spectrum1 Pb

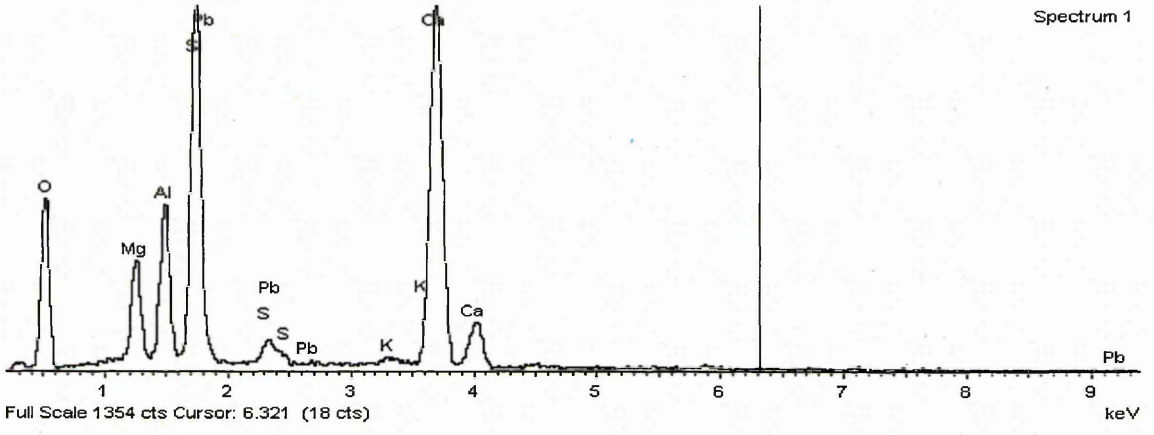

Figure 6.6b EDX analysis for ESEM image 1 of 50ml of 20 000mg/l lead solution stabilised with 0.1g GGBFS, spectrum 1 Pb and associated elements (Pb, Ca, S, K, Mg, Al, and O)

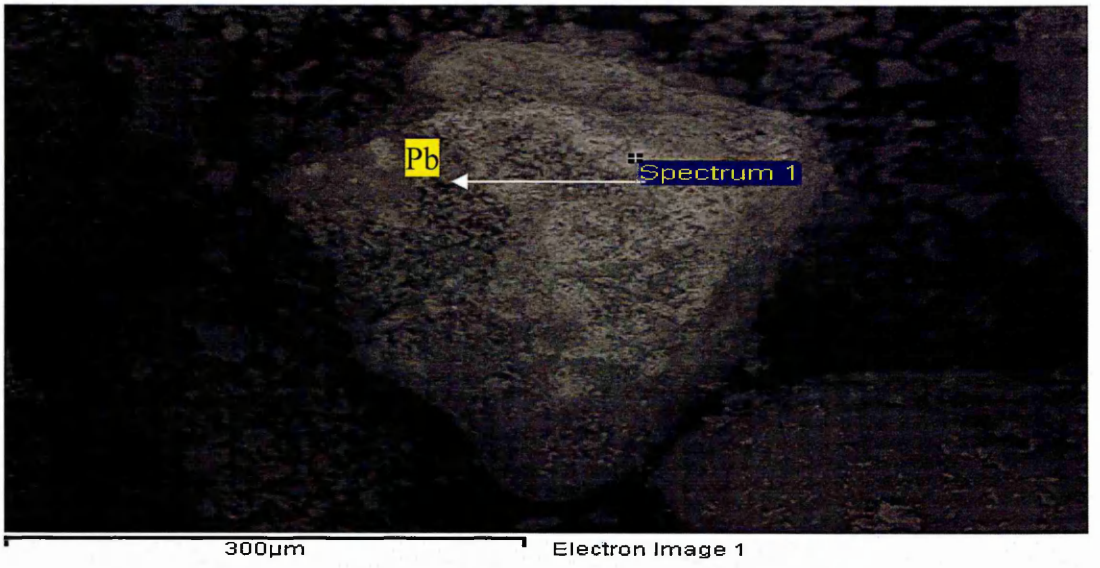

Figure 6.7a ESEM image of lead contaminated soil and lead contaminated soil treated with 0.1g of powder of GGBFS, Spectrum1, Pb

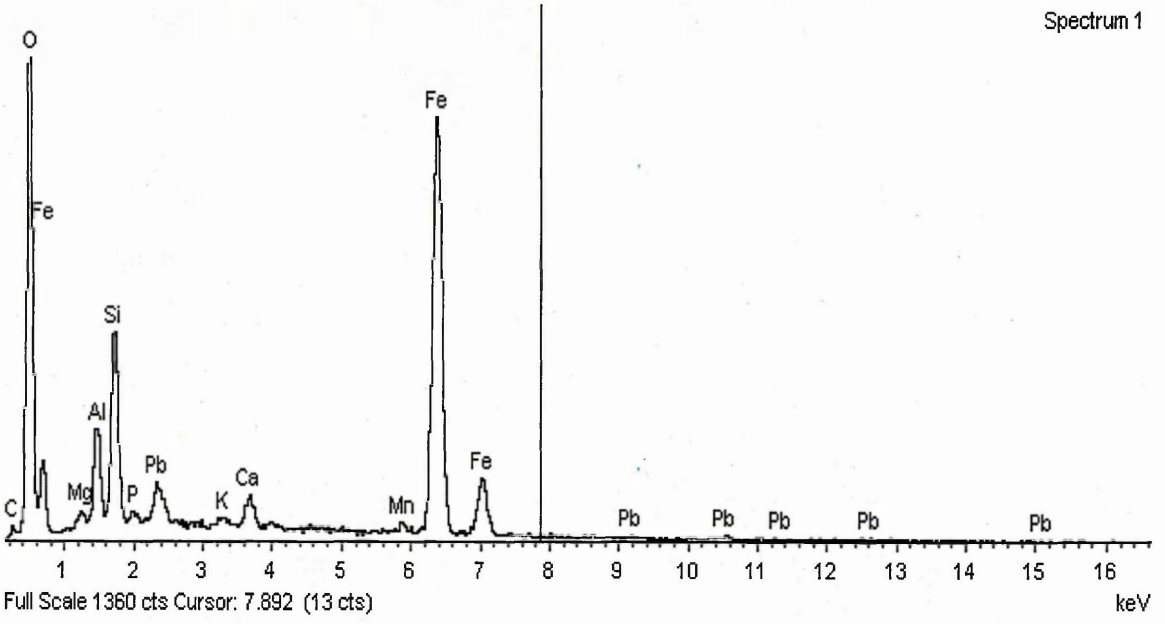

Figure 6.7b EDX analysis of ESEM image of soil contaminated with 50ml of lead solution of 20,000mg/l treated with 0.1 g of GGBFS, spectrum 1 associated elements (Pb, Ca, Mn, Fe, K, Si, Mg, Al, C, and O)

6.3.5 X-ray photoelectron spectroscopy investigation

6.3.5.1 XPS investigations of GGBFS stabilised lead solutions

The results for X-ray Photoelectron Spectroscopy (XPS) analysis for 50ml of lead solution of strength 20,000mg/l treated with 0.1g of GGBFS, is shown in Figure 6.8, which can be compared with Figure 6.9, which shows the analysis for GGBFS with only DI water. The 4f line, which is a feature of Pb is quite clear in comparison with Figure 6.9, which has no lead. Figure 6.8 clearly shows the presence of precipitated Pb on surface of the GGBFS, in agreement with the results of Rha et al [2000] who have reported that lead ions exist mainly on the slag surface. Murakami et al [2000] support this result of formation of those compounds on the surface. Wathiq et al [2003] have also reported the presence of Pb4f in this region of peaks. In other words, Pb ions in a liquid phase did not make inner hydration products of the slag but stayed as a precipitant on the slag surface. In this study, the findings using ESEM, see Section 6.3.5, support this result.

The Pb4f peaks in the spectrum shown in Figure 6.10 are centred on 137.60eV and at 142.5eV. According to accepted international data (http://www.casaxps.com) the peak at 138eV is Pb4f, and at 142eV is $Pb4f_{5/2}$, which could be assigned to PbO, Pb_2O_3, PbS. The type of formation of lead can be in many compounds, see Figure 6.11, which provides an analysis over the Pb4f region. Comparison with Figure 6.12, which is a detailed XPS analysis of the spectrum for GGBFS in DI water over the region of the lead 4f spectral line clearly shows the absence of lead.In the wide scan for the specimen of GGBFS stabilized Pb solution shown in Figure 6.8, the oxygen Ols peak occupied 48.08%, followed by Si2p with 14.37% and C1s with 11.2% of the total mass. The Pb4f peak is well down the list at only 4.49%. Comparison of the peaks of Al2p, Si2p and Ca2p show that their magnitudes all decrease slightly when lead is present, compare Figures 6.8 and 6.9. This observation tends to support the assumption of the reaction of lead with Al, Si or Ca into the GGBFS.

Figure 6.11 confirms that many compounds of lead were formed which are $Pb4f_{7/2}$ and $Pb4f_{5/2}$ Kim et al [2009] have observed Pb4f 7/2 and 5/2 doublets at 140 and 145eV, and reported insufficient information to distinguish PbO from PbO_2 or $PbSO_3$, or even $PbSO_4$, and concluded that the survey scan is sufficient to distinguish metallic lead from the oxidized

forms, according to Singh et al [2010] at 139.28 eV and 145.32 eV, belong to Pb4f 7/2 and 5/2.

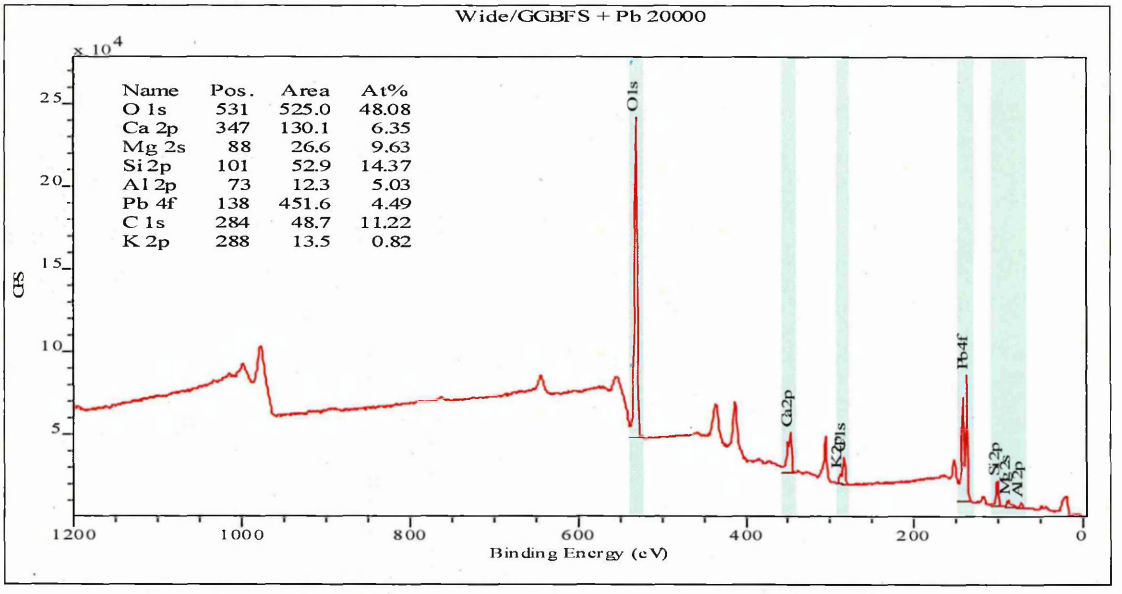

Figure 6.8 Wide scan X-ray Photoelectron Spectroscopy analysis for 50ml of lead solution of strength 20,000mg/l treated with 0.1g of GGBFS

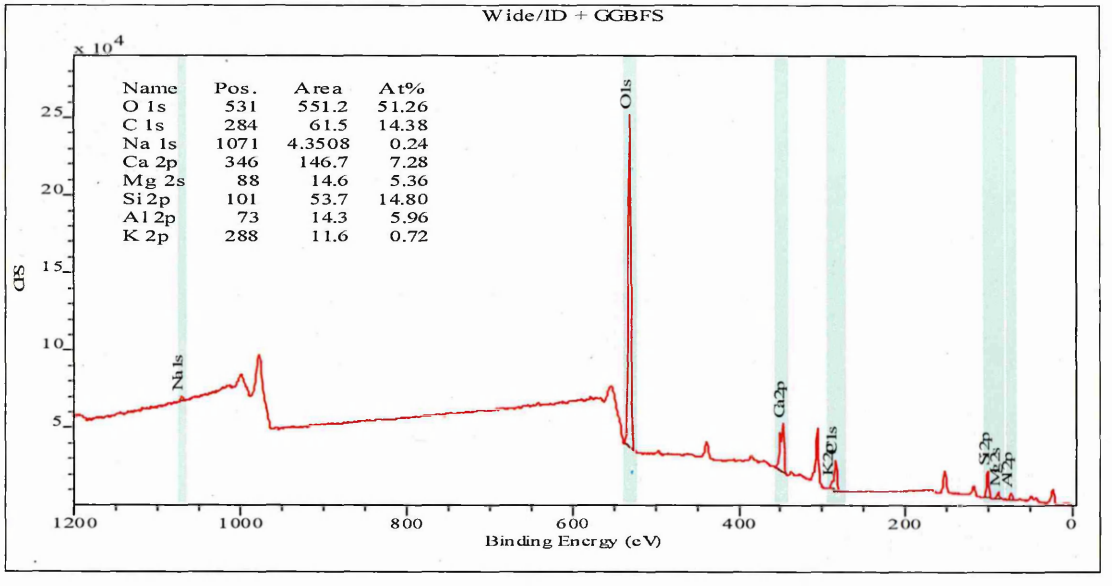

Figure 6.9 Wide scan X-ray Photoelectron Spectroscopy analysis of 0.1g GGBFS in 50ml DI water

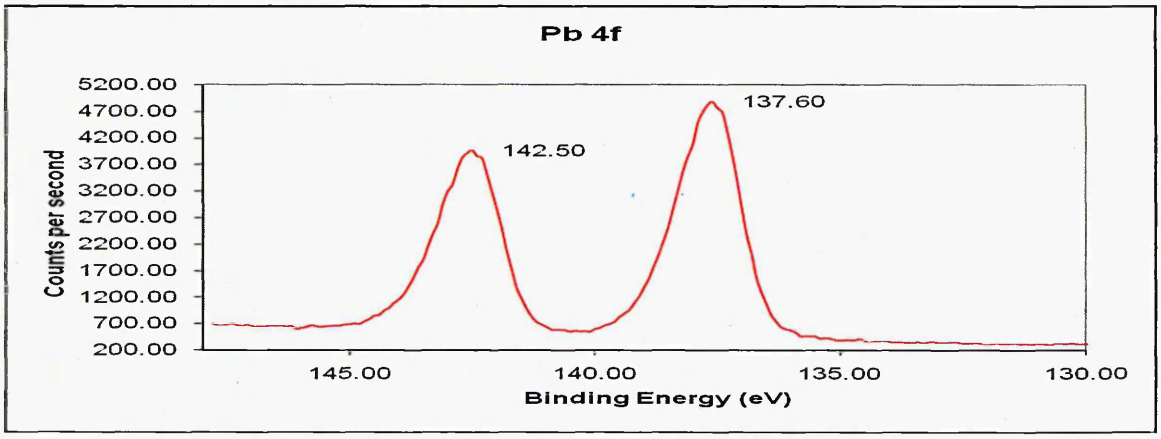

Figure 6.10 Detailed X-ray Photoelectron Spectroscopy analysis of 50ml of lead solution of strength of 20,000mg/l treated with 0.1g of GGBFS in the region of the lead 4f spectral peaks

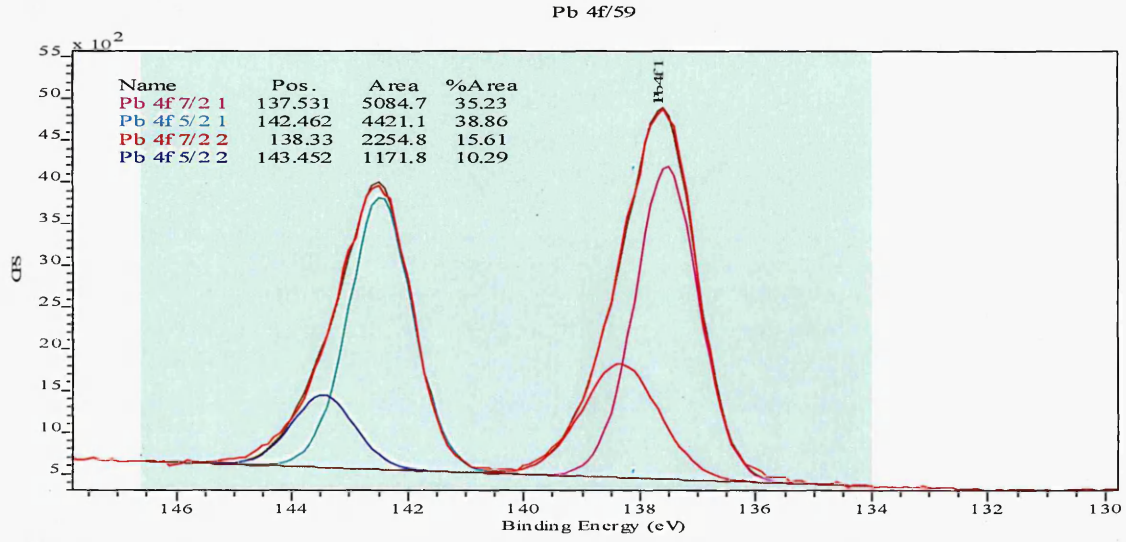

Figure 6.11 Detailed XPS analysis for 0.1 g GGBFS in 50ml of lead solution of strength 20000mg/l, over the region of the lead 4f spectral line

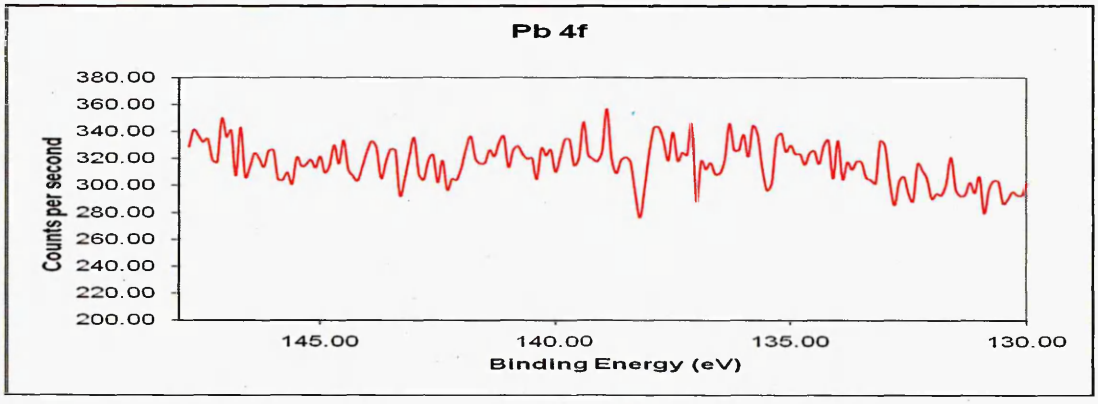

Figure 6.12 Detailed XPS analysis of 0.1g GGBFS in 50ml DI water over the region of the lead 4f spectral line

6.3.5.2 X-ray Photoelectron Spectroscopy for lead contaminated soils treated with GGBFS

A similar procedure was followed for the investigation of treated soil samples as was used for the above investigation of treated lead solutions. Figure 6.13 shows an XPS wide scan for uncontaminated soil, no peak is present which can be attributed to lead. Figure 6.14 shows an XPS wide scan of lead contaminated soil, which clearly shows the presence of lead by the peak at Pb4f, at 136eV. The most common substances were O1s, Si2p and Al2p which accounted for 55.74%, 20.14 % and 7.95% of the contaminated sample respectively. While the peak at 136eV is assigned to Pb4f7 by the XPS international data base, the peak at 141eV is assigned to Pb4f5. James et al [2008] have already classified the chemical state for those peaks, 137eV and 141ev are assigned to PbO or $PbSO_3$.

Figure 6.16 shows the wide scan of contaminated soil treated with GGBFS. Comparison of Figures 6.13, 6.14 and 6.16 for uncontaminated soil, untreated contaminated soil and treated contaminated soil, shows no clear or significant variation in Mg2s or Si2p, a slight decrease in Al2p and a small increase in Ca2p. Going from uncontaminated soil, to untreated contaminated soil to treated contaminated soil, Ca2p rose from to 1.01% to 1.18% to 2.27%. The Pb4f occupied 0.91% and 0.98 % in untreated and treated samples, respectively, which is proof that lead is being bound by GGBFS as confirmed by ICP and ESEM measurements reported in Section 6.3.5.

There was no significant change in Si2p for the three conditions but there was a reduction of Al2p, from 9.64% uncontaminated soil, to 7.95% untreated contaminated soil, to 6.02% in treated contaminated soil. These results support the hypothesis of reaction with Pb which is precipitation of Pb with Si, Al and Ca.etc. Figure 6.17 shows the location of Pb4f peaks in the contaminated soil treated with GGBFS, the peaks in Figure 6.15 which for contaminated soil are similar to treated soils by GGBFS. in Figures 6.17and 6.18 the many compounds of lead formed as a result of adding the GGBFS to the lead contaminated soil, the can be seen. The largest area was occupied by $Pb4f_{5/2}$ and $Pb4f_{7/2}$ which are 38% and 34 % respectively.

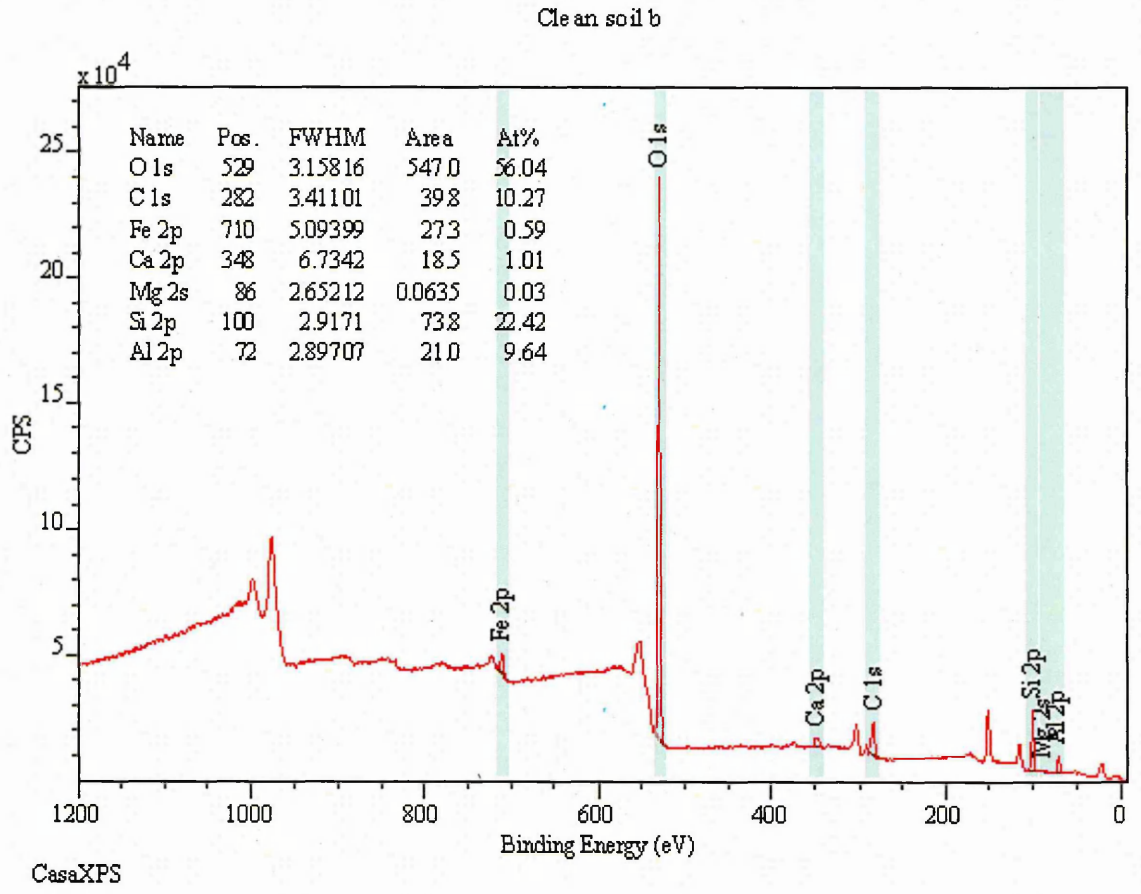

Figure 6.13 Wide scan X-ray Photoelectron Spectroscopy analysis for uncontaminated soil

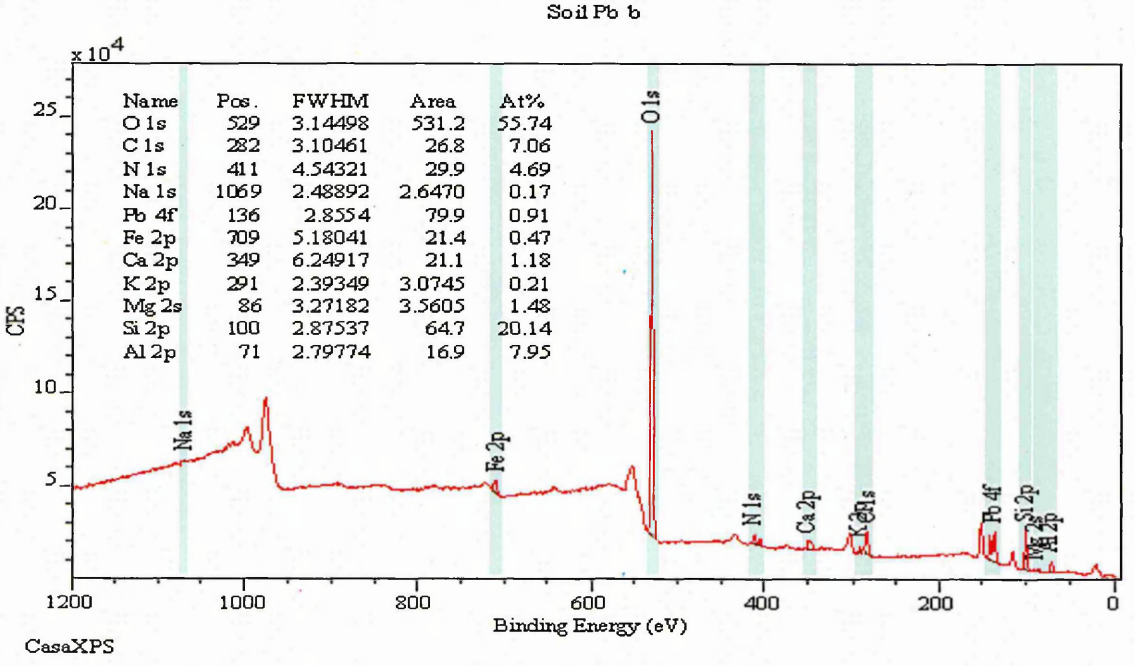

Figure 6.14 Wide scan X-ray Photoelectron Spectroscopy analysis of 5g of soil contaminated with 50ml lead solution of strength 20,000mg/l

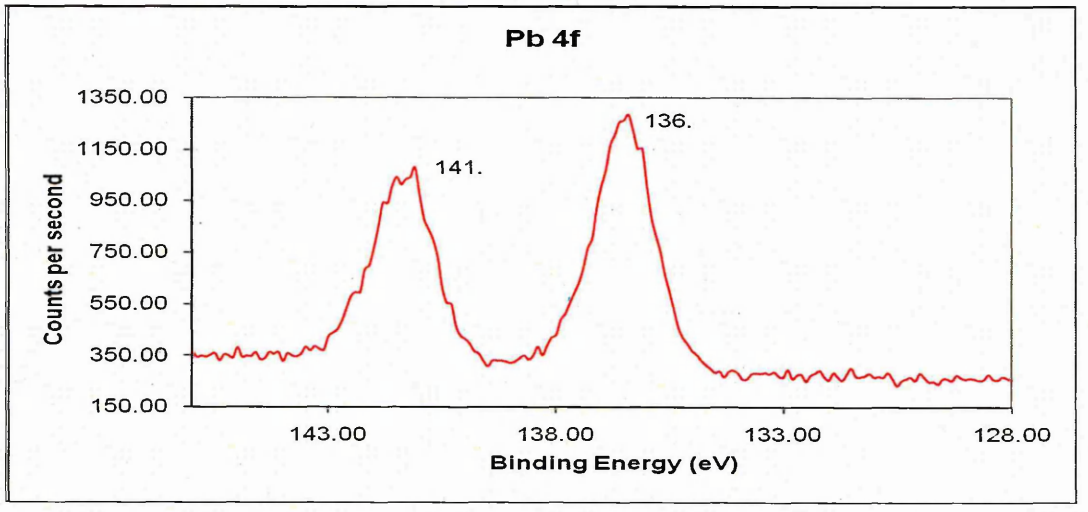

Figure 6.15 Detailed X-ray Photoelectron Spectroscopy analysis of 5g of soil contaminated by 50ml of lead solution of strength of 20,000mg/l in the region of the lead 4f spectral peaks

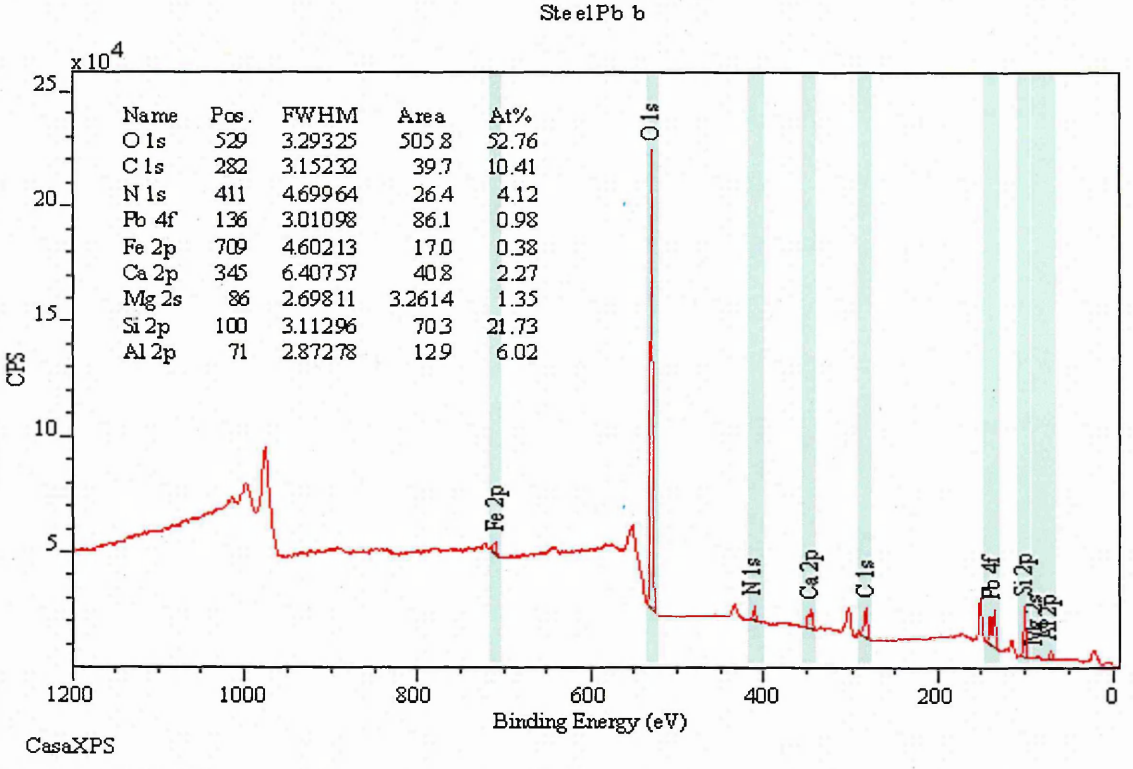

Figure 6.16 Wide scan X-ray Photoelectron Spectroscopy analysis of 5g of soil contaminated spectra with 50ml lead solution of strength 20, 000 mg/l, stabilised by 0.1g GGBFS

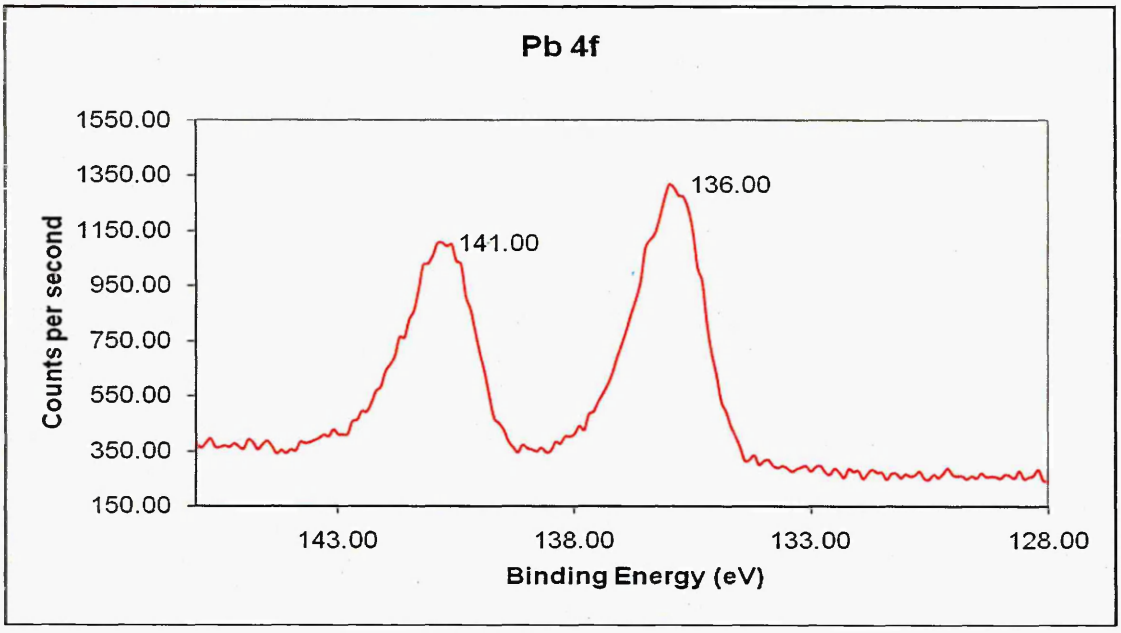

Figure 6.17 Detailed X-ray Photoelectron Spectroscopy analysis of 5g of soil contaminated by 50ml of lead solution of strength of 20 000mg/l in the region of the lead 4f spectral peaks

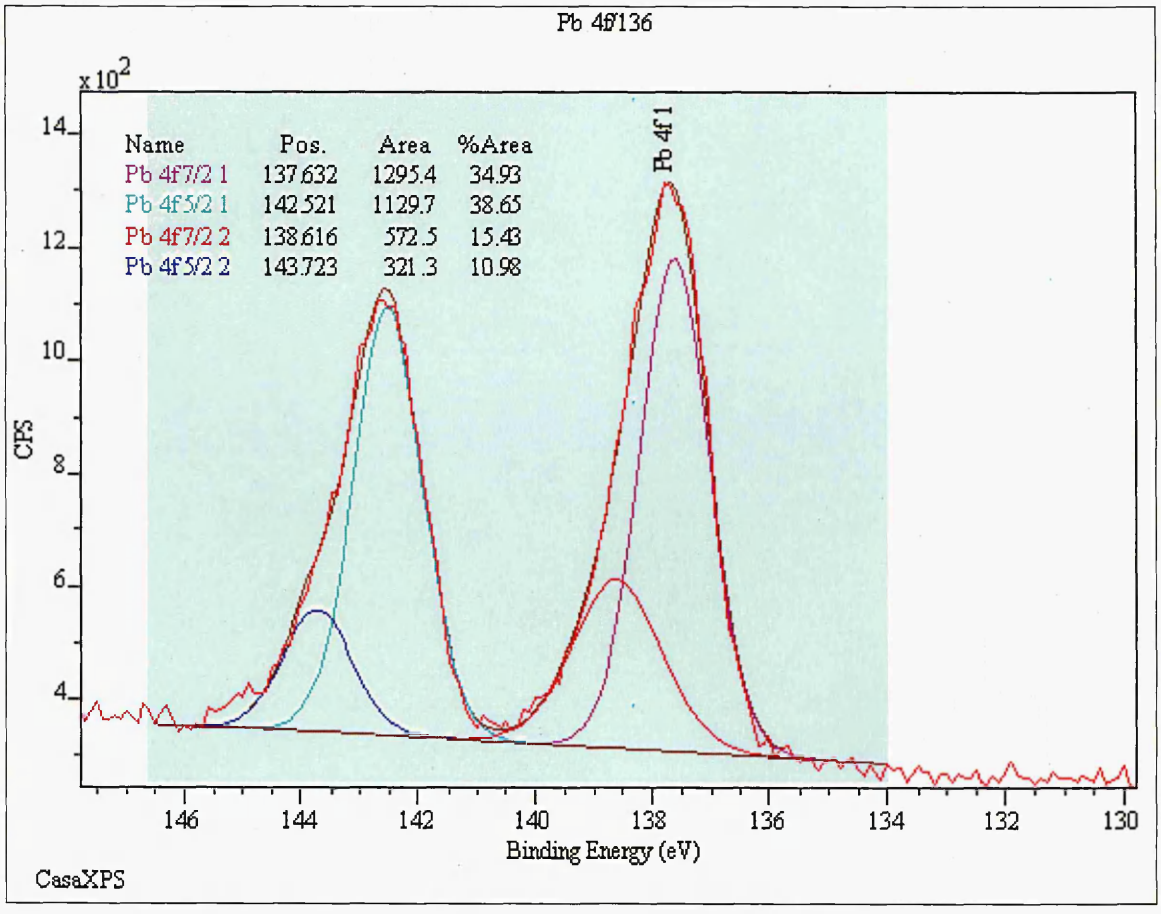

Figure 6.18 Detailed XPS analysis of the spectrum for lime treated lead contaminated soil, over the region of the lead 4f spectral line

6.4 The effect of replacing OPC with 50 % GGBFS on Pb release

Natural materials such as volcanic ash, or industrial by-products such as GGBFS and PFA, are often used as partial replacement for Portland cement in concrete constructions. Resulting advantages include lower environmental impact by reducing waste accumulation, possible improvement in material properties and lower cost. It has been calculated that replacing 5% of the cement presently used by any of the above materials (singly or in combination) could give a reduction of about 75×10^6 tons in world-wide CO_2 emissions [Escalante-Garcia and Sharp, 2004]. Substitutions of cement by GGBFS have been reported as high as 70% Robins et al [1992]. GGBFS has been used in water and wastewater treatments as a low cost adsorbent replacing granular activated carbon (GAC). For example Dimitrova [.2002] and Ortiz et al[2001] have used the GGBFs as an adsorption of nickel, phosphorus and lead

GGBFS (or simply "slag") is a glassy granular material formed when molten blast-furnace slag is suddenly chilled, possibly by rapid immersion in water. It is non-metallic, consisting of silicates and alumino-silicates of calcium, see Table 6.1.The effect of GGBFS adding different proportions of OPC to assist in stabilizing Pb, were carried out using a tank leaching test (see chapter two section 2.3.3 and 2.3.4). The GGBFS was added on a dry basis during the preparation of OPC sample, after mixing and adding contaminated solution, with drops of NaOH were introduced into the mixture of GGBFS and OPC which was poured into the 150mm cubic plastic mould to be cured for 7 days. This followed exactly the procedure for adding PFA to OPC, (see chapter 3 and 7).

GGBFS like Portland cement, is mostly calcium oxide (CaO). In GGBFS this is found associated with calcium silicate, calcium aluminates and calcium aluminosilicate. Although these compounds are not identical to those found in Portland cement (i.e., tricalcium silicate, tricalcium aluminate, etc.), they hydrate when activated by calcium hydroxide, which is one of the by-products of Portland cement hydration. Since GGBFS is almost 100% glassy, it is generally more reactive than most fly ashes. However (slag cement) is generally thought to have many advantages including increased water tightness, suppression of chloride penetration into concrete, resistance to chemical attack by seawater and sulphate ions, reduced heat of hydration, resistance to alkali silica reaction compared to normal Portland cement [Ogawa et al 2008]. Table 6.12 shows how Pb was leached from a cube consisting of 50:50 by weight of GGBFS and OPC. It can be seen from the very small amounts of Pb

which is found in the leachant that this mixture (50%GGBFS+OPC) was much more effective at stabilizing Pb than was OPC on its own, e.g with GGBFS was 0.085g of Pb and at 0% GGBFS was $1.56*10^{-3}$g. [Thevenin and Pera 1999] are in agreement with this result and reported GGBFS cements perform better than OPC cements in stabilising Pb. similarly, [Panesa and Chidiac 2009] also used a mixture containing 50% GGBFS and 50% OPC and reported increased efficiency compared with 100% OPC content especially at scaling resistance at more age than 28 days of curing . [Panesa and Chidiac 2009] reported that several theories have been proposed to explain the surface scaling damage mechanism of concrete, but they all fail to provide a rationale why concrete containing more than 50 % of GGBFS as cement replacement, exhibits poorer scaling resistance as compared to concrete with no or less percentages of GGBFS. However, Duchesne and Laforest, (2004) reported that for a mixture containing 50% GGBFS and 50% OPC, no chromium was leached out, which is in support of results of this study.

Table 6.12 Cumulative release of Pb as function of time during tank leaching test (50% OPC and 50% GBBFs, 50mm cube)

Total duration of immersion of OPC block in leachant (DI water) (hours)	Time between tests (duration of leachant in tank) (hours)	Tank1 Pb (mg/l)	Tank2 Pb, (mg/l)	Tank3 Pb, (mg/l)	Mean Pb (mg/l)	sd	Mean Pb ($\mu g/cm^2$)	Mean Pb $\mu g/cm^2/h$
1	*1*	0.050	N/D	N/D	0.017	0.029	0.071	0.071
3	*2*	0.044	N/D	N/D	0.015	0.025	0.063	0.032
26	*24*	0.176	0.065	N/D	0.080	0.089	0.502	0.024
72	*48*	0.076	N/D	N/D	0.025	0.044	0.104	2.2 x 10-3
120	*72*	N/D	N/D	N/D	0		0	
168	*96*	N/D	N/D	N/D	0		0	
216	*120*	N/D	N/D	N/D	0		0	
Total leached out	0.085 g *$_{10}$-3				0.137		0.57	

N/D=none detected ,Sd= standard deviation

The effect of adding 25% GGBFs to the mix can be seen in Table Appendix 4.1, and it can be seen that the amount of Pb leached out over the test period was substantially less than for 100% OPC.

Dissolution of slag and adsorbed metal ions occurs for either low pH or high temperature. With different pH environments the properties of the slag may change and the release of toxic substances might occur during the leaching process [Ortiz et al 2001]. Thus the reactivity of GGBFS is an important parameter to be considered in the assessment of the effectiveness of GGBFS in concrete composites notwithstanding the findings of Pal et al [2003] that finely ground GGBFS combined with OPC has been found to possess excellent cementitious properties.

For a mixture containing 50% GGBFS the recorded mean pH values was 11.4 at the end of the first hour, an insignificant drop to 11.3 at the end the next two hours, and then a broad peak 11.8 or 11.7 gradually decreasing to 11.4 after the final 48 hours, at which time the cube had been leaching for a total of 216 hours, see Figure 6.19. Interestingly the difference between the mean pH levels for 100% OPC and for 50% GGBFS + 50% OPC are significantly different for all the readings taken (except at 3 hours and 72 hours). There were no significant differences between the pH values for 100% OPC and for 25% GGBFS + 75% OPC. However the pH level at 50%GGBFS in the specimen remain relatively constant .(see Table 6.13 for results of pH in this study) .

Table 6.13 pH level as a function of time (renewable tank leaching test, 50% OPC + 50% GGBFS 50mm cube)

Total duration of immersion of OPC block in leachant (DI water) (hours)	Time between tests (duration of leachant in tank) (hours)	Tank1 pH	Tank2 pH	Tank3 pH	Mean pH	sd
1	*1*	11.2	11.4	11.5	11.4	0.16
3	*2*	11.3	11.2	11.3	11.3	0.05
26	*24*	11.8	11.9	11.8	11.8	0.05
72	*48*	12.0	11.7	11.7	11.8	0.15
120	*72*	11.8	11.7	11.6	11.7	0.11
168	*96*	11.6	11.5	11.4	11.5	0.09
216	*120*	11.4	11.4	11.3	11.4	0.05

Sd=standard deviation

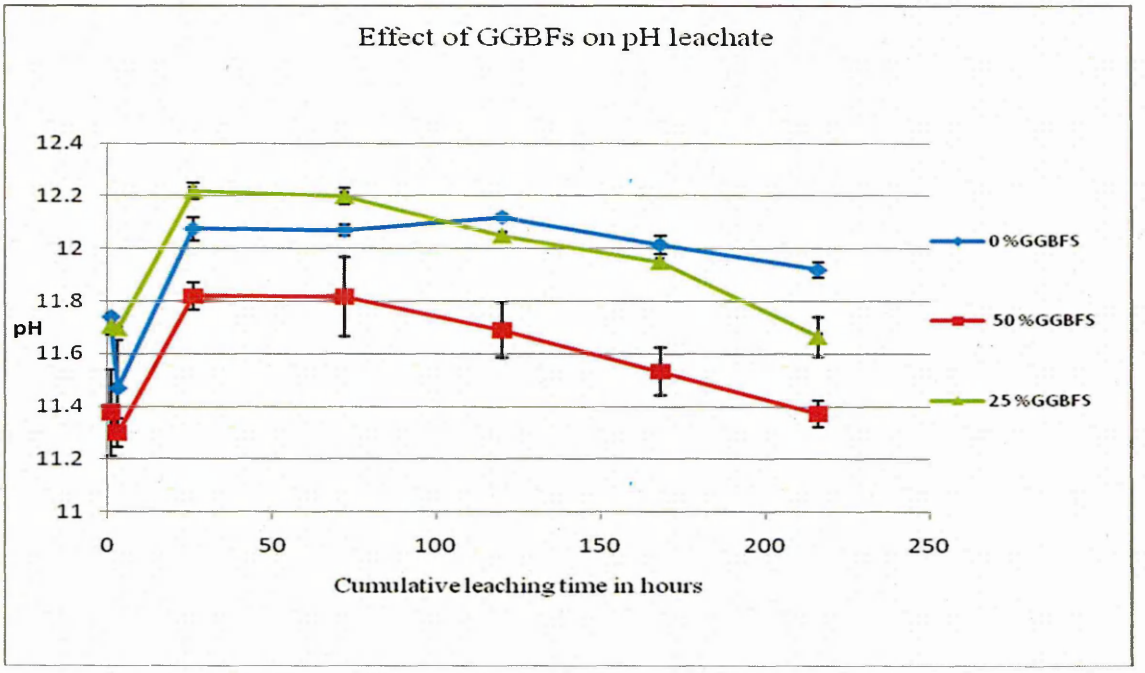

Figure 6.19 Average pH level of leachate as a function of time (renewable tank leaching test, 0%GGBFS + 100%OPC, 25% GGBFS + 75% OPC and 50% GGBFs + 50% OPC)

It is generally assumed that the rise in pH of the leachate occurs due to the dissolution of the $Ca(OH)_2$(portlandite) and calcium–silicate–hydrate (C–S–H) from the cement matrix (Conner, 1993; Cocke et al 1989]. Rapid change of pH can produce marked variation of the solubility of hazardous substances, particularly heavy metals [Lee at al 2006]. The cementitious minerals, which are the major hydration components constituting dominate the solution chemistry of cement–water systems in alkaline conditions. Sanchez et al [2003a], Garrabrants et al [2004] agree with Hinsenveld's (1992) suggestion that $Ca(OH)_2$ dissolves more rapidly than the C–S–H gel. Not surprisingly, the order of reduction in mass is the same as the order of leachate pH increase. The alkalinity of cementitious materials rectifies low pH values of the leachant (normally below pH=5.0) to over 12.0. Since cement–water solutions will be high alkaline environments within a few hours, an interaction of heavy metals with cement components is considered part of the solution utilizing precipitation and adsorption processes.

However, the adsorption capacity of slag is pH dependent and the hydration of slag composition should provide a high pH in the aqueous solutions. Major hydration reactions may occur with calcium oxide, magnesium oxide, calcium silicates, and calcium aluminate [Nilforoushan and Otro 2008].

6.4.1 The effect of replacing 50% OPC with GGBFS on Ca release

Figure 6.20 and Table 6.14 show the release of Ca during the tank leaching test where 50% of the OPC has been replaced with GGBFS. It can be seen that at 50% GGBFS, a significantly lower amount of Ca is leached out compared with only 100% OPC when 5.71 g of Ca leached out, at 50%GGBFS 1.96g of Ca leached out. This is as would be expected because of the low proportion of CaO in GGBFS, only 39 % (see Table.6.1). At the end of the first hour the release of Ca was 751µg/cm^2, this dropped after the next two hours to 592µg/cm^2, thereafter due to the increase in leaching periods the amount leached out increased to 3234 µg/cm^2 for the 48 hour period from 24 h to 72 h. There was than a gradual decrease until the end of the test, for the final 48 hour interval 1477µg/cm^2 was released. However, it should be noted that for a mix of 75% OPC and 25% GGBFS there were no statistically significant differences in the amounts of Ca leached out of the cube. Dimitrova [2002] has reported that high concentrations of calcium in the leachate impeded the uptake of lead. Therefore the mechanism of the removal of lead is ion exchange. The removal process depends on the possibility of releasing calcium ions and their replacement in the slag by lead ions, also the mechanism of precipitation and adsorption occurred in the removal process [Dimitrova ,2002].

Escalante-Garcia and Sharp, [2004] have reported that the release of silicon and aluminium content increased for blended cements, this means there will be considerable changes in the Ca/Si and Ca/Al ratios.

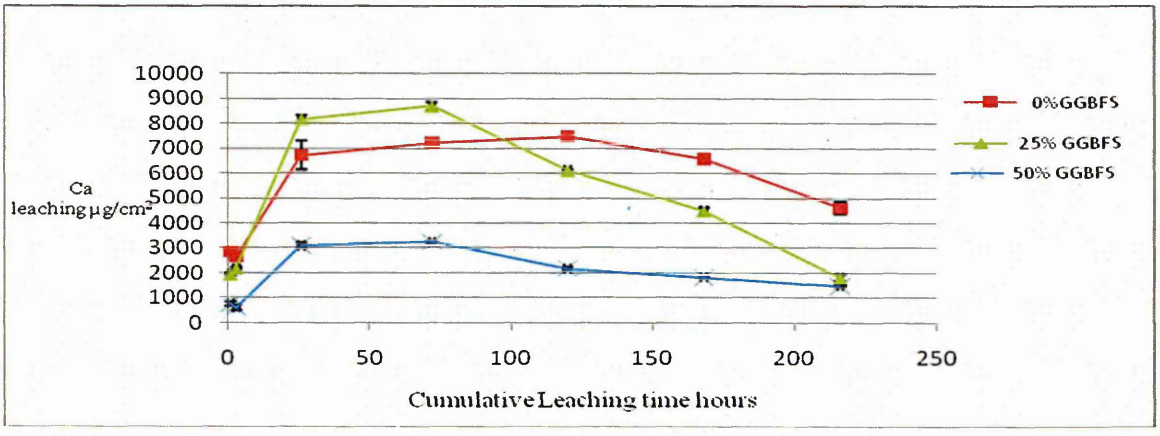

Figure 6.20 Cumulative leaching of Ca(µg/cm^2)at varied time during tank leaching test (100% OPC, 75% OPC + 25% GGBFS, and 50% OPC + 25% GGBFS 50mm cube)

Table 6.14 Release of Ca during tank leaching test (50% OPC + 50% GGBFS 50mm cube)

Total duration of immersion of OPC block in leachant (DI water) (hours)	Time between tests (duration of leachant in tank) (hours)	T ank1 Ca (mg/l)	Tank 2 Ca (mg/l)	Tank3 Ca (mg/l)	Mean Ca (mg/l)	sd	Mean Ca ($\mu g/cm^2$)	Mean Ca $\mu g/cm^2/h$
1	*1*	182	95.6	263	180	83.5	750	750
3	*2*	205	196	25.7	142	101.0	592	296
26	*24*	623	775	826	742	105.6	3090	147
72	*48*	851	774	705	776	72.9	3235	67
120	*72*	477	574	508	520	49.8	2165	45
168	*96*	445	442	421	436	12.9	1817	38
216	*120*	356	396	312	355	42.1	1478	31
Total leached out	**3151*625/1000 mg/l *10 $^{-3}$=1.96 g**				3151		13129	

Sd=standard deviation

However, Yan et al [2000] have described the major hydration reactions with calcium oxide, magnesium oxide, calcium silicates, and calcium aluminate may occur as follows:

$$CaO + H_2O \rightarrow Ca(OH)_2 \quad (1)$$

$$MgO + H_2O \rightarrow Mg(OH)_2 \quad (2)$$

$$2Ca_2SiO_4 + 4H_2O \rightarrow 3CaO \,.\, 2SiO_2 \,.\, 3H_2O + Ca(OH)_2 \quad (3)$$

$$2Ca_3SiO_5 + 6H_2O \rightarrow 3CaO \,.\, 2SiO_2 \,.\, 3H_2O + 3Ca(OH)_2 \quad (4)$$

$$CaO \,.7Al_2O_3 + 12H_2O \rightarrow CaO \,.\, Al_2O_3 \,.\, 6H_2O + 6Al_2O_3 \,.\, H_2O \quad (5)$$

As the slag/cement mix is hydrated it forms less portlandite and thus releases less heat. The C–S–H produced by the GGBFS has a lower Ca/Si ratio than the C–S–H produced by Portland cement [Glasser 1997], which means they have a greater capacity for fixing alkalis and other metals. The GGBFS reacts slowly with water (approximate time 28 days) but its hydration can be activated chemically, thermally or mechanically. If it is possible to allow the slower reacting GGBFS adequate time to react, then the long-term strength of concretes made with this slag is higher than obtained using 100% OPC [Shi and Qian 2000]; Delagrave, 1997). Additionally, the presence of GGBFS decreases the permeability of the cement, thus decreasing the penetration of aggressive agents and increasing the durability of the concrete.

The presence of GGBFS would thus support the long-term capture of heavy metals in the solidified matrix. [Laforest and Duchesne 2005].

6.4.2 The effect of replacing 50% OPC with GGBFS on Na and K release

The release of Na was high at the end of the first hour, 68 μg/cm^2, then dropped to about half that after a further 2 hour interval, the peak was at 24 hours (123 μg/cm^2) after which there was a gradual decrease until 24.4μg/cm^2 for the 48h period ending at 216h, (see Figure 6.21and Table 10 Appendix). There was a significant difference between the amounts of Na leached only for the period after 120 hours. The differences in the release of K for 100% OPC and 50% OPC + 50% GGBFS were significant. The presence of 50% GGBFS significantly reduced the amount of K leached from the cube, (see Figure 6.22 and Table 10 and 11 in appendix).

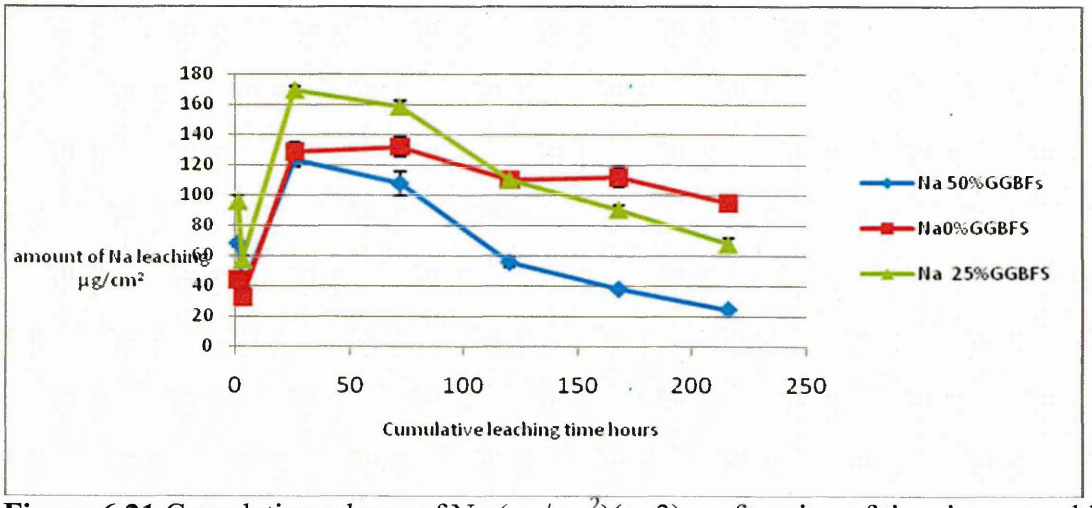

Figure 6.21 Cumulative release of Na (μg/cm^2)(n=3) as function of time in renewable tank leaching test (100% OPC, 75% OPC + 25% GGBFS, and 50% OPC + 25% GGBFS 50mm cube)

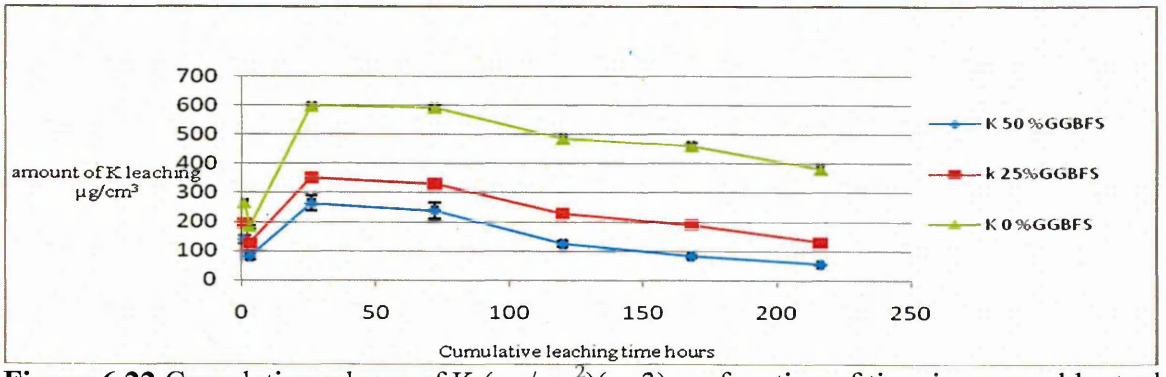

Figure 6.22 Cumulative release of K (μg/cm^2)(n=3) as function of time in renewable tank leaching test (100% OPC, 75% OPC + 25% GGBFS, and 50% OPC + 25% GGBFS 50mm cube)

6.4.3 The effect of replacing 50% OPC with GGBFS on Cl^-, NO_3^-, and SO_4^{2-} release

The general pattern observed with these types of readings is an initial high value after 1 hour, a sudden and substantial drop between 2 and 3 hours, an increase as the time over which the leaching took place suddenly expanded and then a gradual tailing away. There was some divergence in that pattern in these readings because the values measured were so low that small errors could change the pattern.

Figure 6.23 and Table 12 in Appendices. show the data for the leaching of Cl^- .Given the relatively large values of the standard deviations and the small values of the means it is not surprising that there was no significant difference in the results of the leaching tank test for 100% OPC and 50% OPC + 50% GGBFS. However, Panesar and Chidiac [2009] are in agreement with results in this study and reported the chloride capillary suction depth decreases with increasing percentage of GGBFS owing to the blocking of capillary pores by precipitate from chemical binding reactions. At 120 h interval there was large standard deviation in 50 % GGBFS leaching which it can be referred to r error in measurement or driven in calibration of Ion chromatography at end of use.

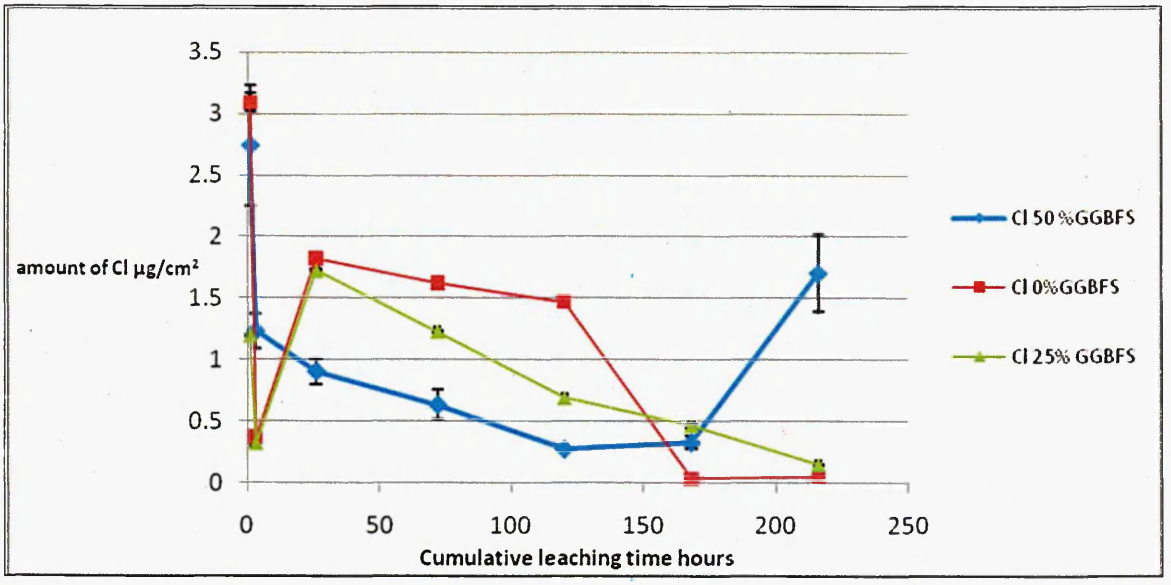

Figure 6.23 Cumulative release of chlorine (µg/cm^2)(n=3) as function of time in renewable tank leaching test (100% OPC, 75% OPC + 25% GGBFS, and 50% OPC + 25% GGBFS 50mm cube)

There was no significant difference in the release of nitrates for the time intervals up to 120 hours. This was because of the large values of the standard deviations (particularly for the 48 hour period to 72h) that occurred with the 50% OPC + 50% GGBFS measurement. However,

for the period after 72 hours the amount of NO_3 leached out is significantly less for 50% OPC + 50% GGBFS than for 100% OPC. At the end of the first hour the total nitrate release was 94µg/cm^2. For the two hour period between the end of the first hour and the end of the third hour the hourly nitrate release was 22.1µg/cm^2/h. The rate of leaching after the next test period was 6.122.1µg/cm^2/h after which it declined gradually, reaching a final value of 0.63µg/cm^2/h. Because of the way the test periods were constructed, there was a peak in the measured values at 24 hours of 127.8 µg/cm^2, after which the measured values gradually declined until after the final 48 hour period reached 30µg/cm^2, see Figure 6.24 and Table 13 in appendix.The lower rate at which the NO_3 was leached out after 72 hours is put down to the large amount of GGBFS in the specimen and the adsorption capacity of GGBFS for NO_3 .

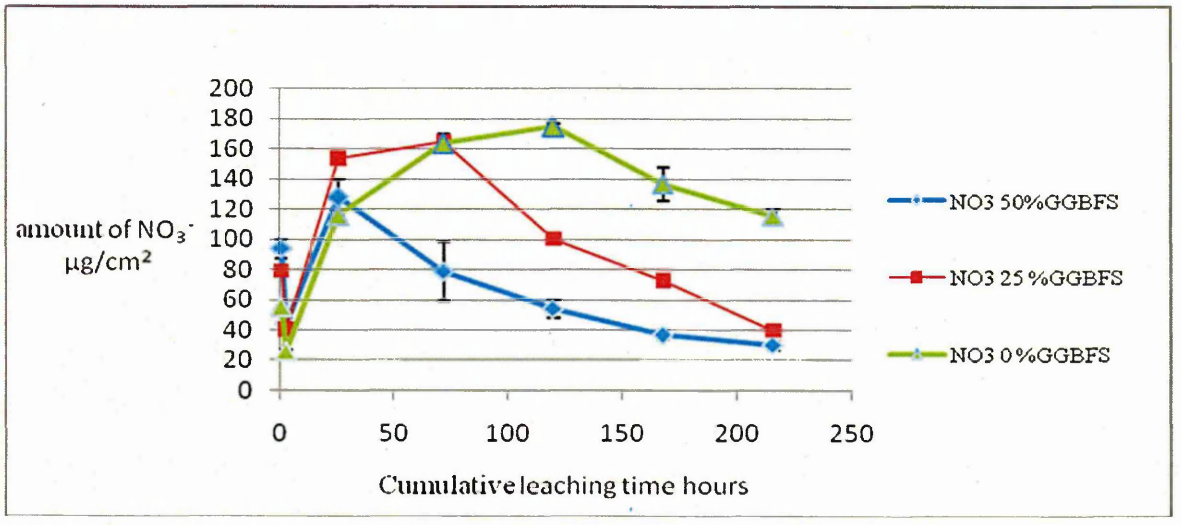

Figure 6.24 Cumulative release of nitrate (µg/cm^2)(n=3) as function of time in renewable tank leaching test during tank leaching test (100% OPC, 75% OPC + 25% GGBFS, and 50% OPC + 25% GGBFS 50mm cube)

No significant differences were noted between levels of SO_4 leached from the 100% OPC cube and the 50% OPC + 50% GGBFS cube. The hourly rates began at 43.2µg/cm^2/h for the first hour, dropped to 4.37 µg/cm^2/h over the next two hours and then remained more or less constant (at least within experimental error) for the remainder of the test period. Because the test periods were not equal there was a peak at 24 hour reading of 10.6 µg/cm^3 ,see Figure 6.25 and Table 14 in appendix.

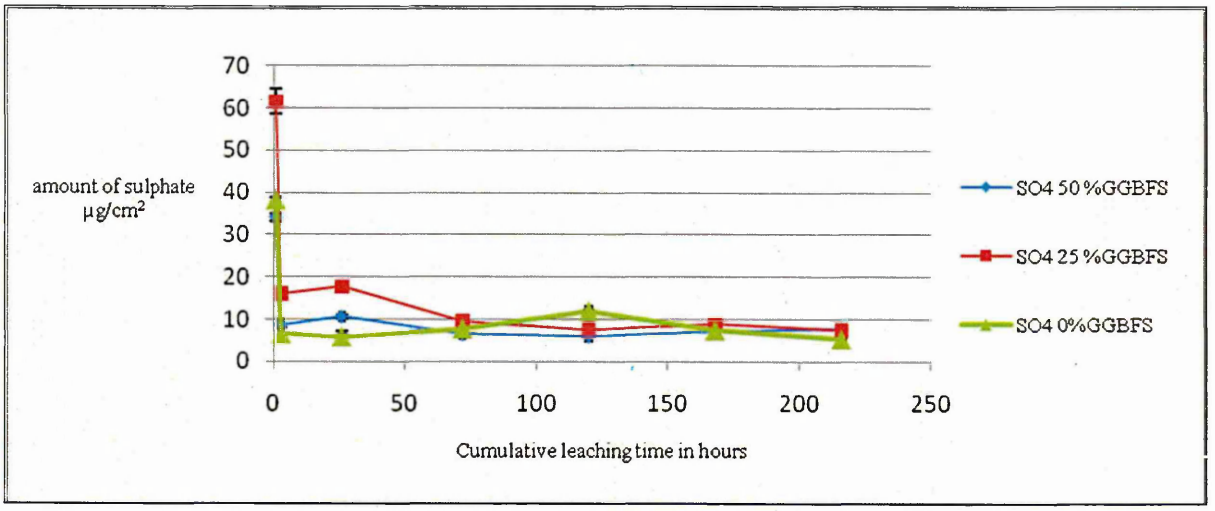

Figure 6.25 Cumulative release of sulphate (µg/cm^2)(n=3) as function of time in renewable (100% OPC, 75% OPC + 25% GGBFS, and 50% OPC + 25% GGBFS 50mm cube)

Chapter Seven

Effect of PFA on metal contaminated soils and solutions

7.1 Methods for measurement of the leachibility of lead

The leachability of lead was determined in a similar manner to that described fully in Section 2.2.4.

7.2 Composition of fly ash and effects on metal contaminated solutions and soils

Fly ash, or pulverised fuel ash (PFA) as it is known in the UK, is a by-product of coal-fired power generation and has been used for a wide range of applications for over 50 years. For example, Wang and Hongwei [2006], Weng and Huang [2004], Alinnora, [2007] and Pehlivan and Cetin [2008] have all shown that PFA may be used in wastewater treatment, particularly for adsorption, because of its major chemical components, such as alumna, silica, ferric oxide, calcium oxide, magnesium oxide, and carbon, and its physical properties, such as porosity, particle-size distribution, and specific surface area. However, Gatima et al [2005] has pointed out that it is important to consider the source of the PFA, as certain sources may contain toxic elements (especially Cd, Cu and Pb), defeating the primary purpose of amelioration.

PFA is often incorporated into solidification additives [Cote et al., 1987; Conner, 1990; Awe et al. 2001 and Qiao et al 2006]. The finer fraction of PFA (<451 μm, as measured by sieving) chemically reacts with $Ca(OH)_2$ at ordinary temperatures to form cementitious hydration products and so PFA and cement can be used in the stabilisation/solidification (S/S) of hazardous wastes, where it has economic, technical and energy-saving advantages [Lee et al., 1991; Qiao. et al 2006]. However, Tsadilas et al [2009] argues that the effects of PFA when it is applied to soils for heavy-metal adsorption, especially through pH increase, have not been adequately investigated. With the recent upsurge of interest in the impact of industry on the environment, some e.g. Gatima, et al [2005] have questioned the use of PFA as an adsorbing material when applied as an ameliorant in treatment effluents and have re-stated how important it is to investigate the source and composition of PFA prior to its use for remediation purpose.

There are many reasons to increase the amount of flyash being utilized, which are: firstly, disposal costs are minimized; secondly less area is required for disposal, thus enabling other uses of the land and decreasing disposal permitting requirements; thirdly, there may be financial returns from the sale of the by-product or at least an offset of the processing and

disposal costs; and fourthly, the by-products can replace some scarce or expensive natural resources,[Ahmaruzzaman 2010].

The composition of the ash is one key variable determining its reactivity. Fischer et al., [1978] analysed the two main types of fly ash (types C and F) produced from coal combustion. Type F is produced from the combustion of anthracite, bituminous or sub-bituminous coal and contains less than 7% lime but contains more alumina, iron and silica oxides. Type C comes from lignite coal produced from burning sub-bituminous or lignite coals and contains between 15 to 30% lime. These two types of fly ash are commonly used in concrete class C are often high-calcium fly ashes with carbon content, less than 2%; whereas, Class F are generally low-calcium fly ashes with carbon contents less than 5% but sometimes as high as 10%. In general, performance properties between Class C and F ashes vary depending on the chemical and physical properties of the ash and how the ash interacts with cement in the concrete. Many Class C ashes when exposed to water will react and become hard just like cement, but not Class F ashes. Most, if not all, Class F ashes will only react with the by products formed when cement reacts with water. Basham et al.[2007].Although both types of fly ash impart a wide range of qualities to many types of concrete.

The chief difference between Class C and F fly ash is in the amount of calcium and the silica, alumina and iron content in the ash. In Class F fly ash, total calcium typically ranges from 1 to 12%, mostly in the form of calcium hydroxide, calcium sulphate, and glassy components, in combination with silica and alumina. In contrast, Class C fly ash have reported calcium oxide contents as high as 30–40%. Another difference between Class C and Class F is that the amount of alkalis (combined sodium and potassium), and sulphates (SO_4^{2-}), are generally higher in the Class C fly ash than in the Class F fly ash, which is especially useful in soil stabilization since class C may not require the addition of lime. [Ahmaruzzaman 2010], However. fly ashes are considered pozzolans because they contain silica and alumina, and when the silicate phases have an amorphous, rather than crystalline structure, these pozzolanic materials can contribute to the formation of hydration products, when attacked by hydroxides. Nonavinakere and Reed [1995] have shown that the silica present can react with the calcium hydroxide released by hydration of calcium silicate to produce calcium silicate hydrate [Iyer and Scott 2001].

$2\ Ca_3SiO_5 + 7\ H_2O \longrightarrow 3\ CaO \cdot 2\ SiO_2 \cdot 4\ H_2O + 3\ Ca(OH)_2$ + energy .

The composition of PFA is different from that of GGBFS, Tables 6.1 and 7.1, as can be seen from Table 7.1 the PFA consisted of Al, Si and a small amount of CaO, so it can be classified as zeolite. Li. et al., [2007] have shown that zeolites, because of their chemical and structural characteristics, cation-exchange capacities, adsorption and alkaline pH, are widely used in contaminant immobilization chemically.

Table 7.1 Chemical composition (by mass %) for PFA and uncontaminated soil

Compound	pH	CaO	Al_2O_3	SiO_2	MgO	P_2O_5	SO_3	K_2O	TiO_2	Fe_2O_3	Na_2O	BaO
Fly Ash	0.1g of PFA + 50ml DI water =9.5	2.09	26.01	49.2	1.5	0.24	0.35	3.45	0.94	9.16	1.18	0.15
Uncontaminated soil	0.1g of soil + 50ml DI water =6.9	0.12	2.89	93.6	0.13	0.02	0.06	1.72	0.08	0.65	0.21	0.03

Y_2O_3, V_2O_5, ZrO_2 , Cr_2O_3, ZnO , Mn_3O_4 and SrO were not detected in the uncontaminated soil and were present to less than 0.06% in the fly ash solution.

The composition of PFA will vary with the quality of coal used and the operating conditions of the power station. In this study the composition of fly ash was determined by XRF; the main components were SiO_2 (about 50%) and Al_2O_3 (about 26%); the next three most common components in order were Fe_2O_3 (about 9%), K_2O (between 3 and 4%) and CaO (about 2 %), see Table 7.1. These results concur with those of e.g. Gatima et al [2005] who found that, typically, about 95-99% of fly ash consisted of oxides of Si, Al, Fe and Ca, and about 0.5 to 3.5% consisted of Na, P, K and S with the remainder composed of trace elements. Erol et al., [2005] suggest that the principal oxide constituents of PFA can be divided into those that are acidic (SiO_2, Al_2O_3 and TiO_2) and those that are basic (Fe_2O_3, MgO, CaO, Na_2O and K_2O). Gatima et al [2005] also used PFA for amelioration of lead contaminated soils and achieved good results in reducing the levels of lead below the regulatory limit for soils contaminated with different lead compounds, included $PbNO_3$.

When PFA is added to water, the solution initially has a low pH as sulphate on the surfaces of the particles enters into solution as sulphuric acid. However, after a short time, calcium is leached into solution and the pH rises rapidly to 9-12. Typically, for PFA the pH is between 8 and 11, but for those ashes with a higher free calcium oxide content the pH can rise to 12. In fact, very little free calcium is required to achieve the higher pH. For PFA that has had most of the water soluble content washed out e.g. lagoon ash or pond ash , a significant proportion of the material that influences pH will have been removed and the pH is lower, typically

around 9 [Lindon. et al 2003]. In this study after shaking for two hours in Di water the PFA solution was 9.5 (see Table 9.5).

7.2.1 Effects of fly ash on lead solution

Pb^{2+} removal capacities have been related to the CaO contents of the fly ash, which would dissolve in water and so increase the pH number. However, the content of CaO in the fly ash is only 2 %(see Table 7.1).When 0.1g of PFA powder was mixed with 50 ml of DI water, the average pH was 9.5, see Table 7.2. Erol et al[2005] studied the four parameters which affected the removal of Pb from solution which are, contact time, fly ash composition, fly ash concentration and the pH of the solution, as might be expected, that the pH value increased with the increases in concentration of the PFA. And they reported that maximum removal of Pb at pH 6-7 with using varied samples of fly ash was between 0.075–3.5 g/l.

Table 7.2 Measured pH when 0.1g PFA powder was added to 50ml of DI water and to 50ml of 1000mg/l) $(PbNO_3)_2$ solution(n=3)

sample	pH	Mean	Sd
50 ml of D.I water + 0.1g of PFA	9.45		
50 ml of D.I water +0.1 g of PFA	9.58	9.5	0.078
50 ml of D.I water + 0.1g of PFA	9.44		
1000mg/l solution of $PbNO_3$	3.54		
1000mg/l solution of $PbNO_3$	3.55	3.5	0.005
1000mg/l solution of $PbNO_3$	3.55		
50ml of 1000mg/l solution of $PbNO_3$ + 50 ml of D.I water + 0.1g of PFA	4.78		
50ml of 1000mg/l solution of $PbNO_3$ + 50 ml of D.I water + 0.1g of PFA	4.71	4.7	0.085
50ml of 1000mg/l solution of $PbNO_3$ + 50 ml of D.I water + 0.1g of PFA	4.61		

Fig. 7.1 shows the effect of increased pH on reduction of lead in the final leaching solution. At a pH number of about 6.5 the lead concentration was reduced to 0.5mg/l. From Fig. 7.1 it is obvious that fly ash on its own has no effect on the concentration of lead in the final solution, However, if even a small amount of NaOH (just a drop – 100 μ micron of a 2 mole solution of NaOH) is added with the 0.1g of PFA powder, the concentration of lead in the final leaching solution was substantially reduced.

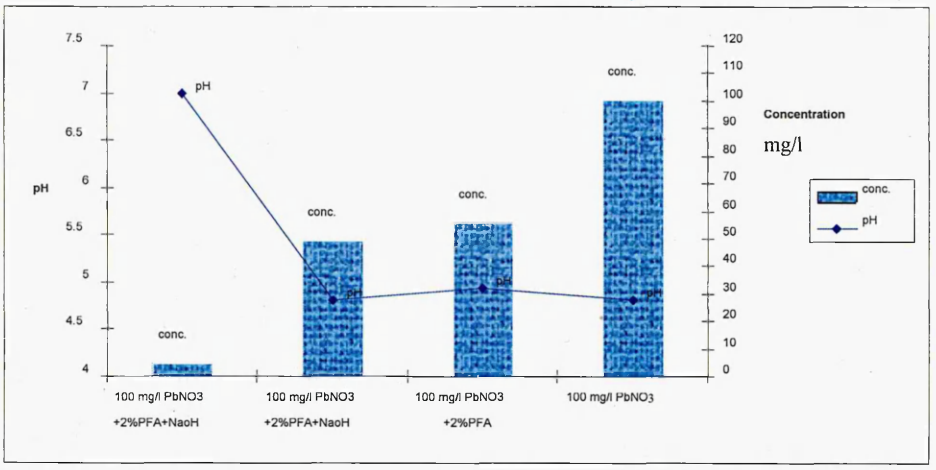

Figure 7.1 Effect additions of NaOH and PFA on concentration of lead in solution

In the Fig.7.1 the uptake of lead was strongly affected by solution. At the initial lead concentration of 100 mg/l, lead removal efficiency was zero at a solution pH of 3.5, but it increased sharply when solution pH rose from 3.5 to 6.2.The conclusion to be drawn from Fig.7 .1 is the same as that of Erol et al [2005] on its own PFA has little or no effect on the stabilization of the lead solution. As can be seen in Fig.7.1 there was no decrease in the final lead concentrations after the addition of PFA nor was there any change in the pH in the final solution. But it is not the only factor in removing the lead, the adsorption capacity of PFA has an effect on remove the lead for solution and soils under certain conditions, similar to study reported by Zhan and Zhao [2003].

Erol et al [2005] carried out parametric studies on the retention of Cu, Zn and Pb from aqueous solutions using PFA, which included the effect of parameters of adsorption of metal by fly ash. These included the amount of ash, to pH, the initial concentration and temperature [Bayat 2002]. Kasprzyk and Kordylewski [2006] have compared the adsorption capacities of silico-aluminous and sulpho-calcic, ashes produced by circulating fluidised bed combustors (CFBC). Alinnora[2007] has shown that the uptake of Pb^{2+} ions decreases when the pH value of the leaching solution increases from pH 4 to pH6. At a pH of 4 about 81.9% of Pb^{2+} ions were removed from solution by the PFA and for a pH of 6 the proportion removed fell to 77.6%. As the pH value increased above pH 6, there was a gradual increase of Pb^{2+} ion uptake up to pH 10 ,it maximum removal of Pb^{2+} was removed at this pH 9-10, which then remained almost constant up to pH 12. In general, the amount of heavy metal ions removed from solution increased as the pH increased, although this was not a monotonic increase.

Li. et al., [2007] have examined cation exchange of metal ions, with Na^+ or K^+ ions of zeolite precipitating heavy metals as low-solubility hydroxides, due to the increase of the solution pH by zeolite addition. They suggest that the mechanisms taking place are the adsorbing or absorbing of the heavy metals on the surfaces or in pores which is support for another application of PFA in its use in removing metal ions.[Gatima, et al 2005] and also phenols from water, due to its adsorption capacity.[Alemany et al 1996].

7.2.2 Effect of PFA on 100mg/l solution containing Cu, Pb, Cd, Ni, and Cr

The solution of metals was prepared as described in Section 2.1.4. Table 7.3 shows the introduction of PFA to the metal solution had no effect on the reduction of concentration of metal in solution, nor was there any change in the pH of the final solution. The pH was 3.3 in the presence of PFA. The behaviour of Pb in the presence of PFA is the same whether or not other metals are present. Only 10 % reduction of Pb concentration by the leach solution was found after batch test for 2 hours duration and 0.1g PFA added to 50ml or 100ml of Pb solution, individually or combined with other metals, see Table 7. 3.

Zhan and Zhao [2003] reported that the maximum uptake of lead and chromium took place at pH 6.0 and 5.0, respectively. It is also apparent from this work that the adsorption rises from 1.4 mg/l (pH 2.0) to 3.8 mg /l (pH 6.0) for lead and 0.8 mg/l (pH 2.0) to 1.8 mg /l (pH 5.0) for chromium and then starts to decrease in both cases. The decrease of the adsorption at higher pH may be attributed to the hydroxide formation of lead and chromium.

In Table 7.3 the reduction of Pb was only 10 %, and Ni +Cr were 4%, no effect of Cd or Cu concentration. The final pH was increased by 0.3 pH unit, compared to the blank solution with no PFA, which is pH 3.08. The results of Bayat [2002] agreed with this initial pH of 3 and reported final pH in range of 3-8. Also Ricou.et.al [1999] reported that for pH less than 3, a small adsorption capacity is found between the metal cation and hydrous ion confirming the importance of pH control to remove the metals from solution. The mechanism of metal removal at pH >6 is precipitation, 6<pH<5 adsorption and surface, pH<competitive adsorption H_2O. The observed amounts of removal during the current study were 7%, 44% with wet fly ash at constant pH as the amount of fly ash increase.

Table 7. 3 The Effect of PFA on a mixture of five metals in solution: Cu, Pb, Cd, Ni, and Cr, concentration 100mg/l and 50ml of metals, solution.(n=3)

Sample	pH	Pb (mg/l)	Ni (mg/l)	Cd (mg/l)	Cr (mg/l)	Cu (mg/l)	Cl (mg/l)	NO_3 (mg/l)	SO_4 (mg/l)
0.1g of PFA Powder + 50ml of 100 mg/l Metal Solution	3.3	89.3	96.6	102.9	95.9	98.1	7.7	1559	23.5
0.1g of PFA Powder + 50ml of100 mg/l Metal Solution	3.3	89.2	94.8	100.9	95.4	99.4	8.05	1533	20.3
0.1g of PFA Powder +50 ml of 100 mg/l Metal Solution	3.2	93.7	96.8	99..2	98.3	100.1	8.1	1542	24.4
Mean	3.3	90.7	96.1	101.0	96.5	99.2	7.95	1545	22.7
Sd	0.05	2.56	1.10	1.90	1.55	1.01	0.21	13.1	2.15
50ml of100mg/l metal solution	3.08	100	100	100	100	100	Nd	Nd	Nd
50 ml of 100mg/l metal solution	3.07	101	100	100	100	100	Nd	Nd	Nd
50 ml of 100mg/l metal solution	3.09	100	102	101	99	101	Nd	Nd	Nd
Mean	3.08	100	101	100	100	100			
Sd	0.01	0.0	0.01	0	0	0			

sd=standard deviation ,Nd=no detection

Bayat[2002] reported that the fly ash sorbent effect in depended on CaO content as active carbon to removal the Ni and Cu and concluded that the maximum metal removal was found to be dependent on solution pH (7.0–8.0),for Ni (II), 5.0–6.0, for Cu (II) and 6.0–7.0 for Zn(II)

Hui et al,[2005] used 0.5 g of fly ash and reported high capacity to remove the metal ions (Cr^{3+}, Cu^{2+}, Zn^{2+},Ni^{2+} and Co^{2+}) from solution with pH range of 3-5, the contact time was 2 hours, and element were prepared from salts. The maximum concentration was 300 mg/l. These authors concluded that the removal mechanism of metal ions was by adsorption and ion exchange processes. Cetin and Erol.[2007] reported that the maximum metal removal was found to be dependent on solution pH 4.0 for Ni(II) and Zn(II). The sorption of metal ions increased with an increase a pH, and maximum removal was obtained at pH 5.0 for fly ash with 97.2% and 78.2% removal for Cu^2C and Ni^2C ions, respectively. The fly ash consisted of silica (SiO_2), alumina (Al_2O_3), and iron oxides (Fe_2O_3), with varying amounts of carbon, calcium, magnesium, and sulphur. The fly ash was found to be a metal adsorbent as effective as commercial activated carbon.

Hsu et. al [2008] has observed the removal of Cu at pH 5 as a results of participation of Cu on the surface of ash using 0.1 g of fly ash, which is similar to this study, shaking for 24 h, with a concentration of 40 -400 mg/l $Cu(NO_3)$.

However it is noticed the amount of SO_4^{2-} and Cl^- released (see Table 7.3) were higher 22 mg/l and 7.1 mg/l respectively compared with adding GGBFS or lime to Pb solution, due to the amount of sulphate being generally higher in PFA.

The extremely high capacities of fly ash for Cu (II) and Pb (II) may be attributed to the contribution of surface precipitation. Apak et al,[1999] also observed that fly ash with a high CaO content was shown to be effective for Ni(II), Cu(II) and Zn(II) removal from aqueous solutions. The adsorption in these systems is highly dependent on pH, initial metal concentration and fly ash origin. The effects observed were: increase in metal removal with increasing solution pH (up to pH 6.0 for Cu(II), pH 7 for Zn(II) and pH 8.0 for Ni(II)), the pH for Ni(II) is slightly in disagreement with Bayat.[2002],who reported pH for Ni(II).

Hulya et.al.[2007] reported the ability of the sorbents to remove a mixture of As, Cd, Cr, Cu, Ni and Zn from synthetic storm water under controlled pH 6.5.With using 1 g of PFA into 50 ml of metal solution and initial concentration of 20g/l, shaking for 48 h, with initial pH 6.5,they reported precipitation of metal consequently, PFA had high affinity for Ni, Zn, Cu and Cd, which at the high pH during the experiments with PFA mainly are present on charged or anionic species (i.e. $Ni(OH)_2$, $Zn(OH)_2$, $Cd(CO_3)_2$, $Cu(CO_3)_2$.

Mishra and Patel [2009] reported adsorption of lead and zinc under similar condition at different pH. There is practically no removal at pH lower than 3 may be due to high H^+ ion concentration, which reverses the process of adsorption. There was a gradual increase in adsorption with increase in pH from 3 to 6 and the maximum adsorption was at pH 6. Again the percentage of adsorption increases gradually with increase in pH from 6 to 10 and may be due to the formation of the precipitate of $Pb(OH)_2$ and $Zn(OH)_2$. Thus pH 6 was considered as the optimum condition and was used for further study for both single and binary systems.

7.2.3 Effect of adding PFA to contaminated soils

While performing the batch leaching test on soil contaminated with Pb (see Section 2.7) in which 0.1g of PFA was added to the 5g soils and 50ml of DI water was added. The reduction of lead in the soil was from over 80µg/g with no PFA to nearly 0µg/g when 2% PFA was added, representing a reduction of about 95%. Figure 7. 2 shows the effect of no PFA, 0.5%, 1.0%, 1.5% and 2.0% to the contaminated soil. Increasing the %PFA progressively reduced the lead remaining in the soil. This means that there is no retention of lead in the soil. Figure 7.3 shows the proportional reduction of lead in the soil with %PFA. The amount of lead in soil was 1000mg/l and maximum extraction were achieved by using a digest test 780 µg/g,(see section 2.1.5). The extraction of Pb by using shaking test for two hours and DI water as leaching fluid is 80 µg/g. The 0.5% of PFA is equivalent to 0.25 g of PFA, which was the minimum amount of PFA used to assess reduction in Pb release. It was observed during measurement of the pH at the end of the shaking batch test that the pH level of the final filtered solution increased as the %PFA increased (see Table 7.4). Kumpiene et al [2007] used PFA to mobilize the Cu and Pb and achieved 95 and 99% reduction of Pb. Erol et al [2005] reported that the amounts of PFA required to remove Cu^{2+} and Pb^{2+} were found to vary between 0.2–10g/l and 0.075–3.5g/l, respectively. Moon and Dermatas [2007] used 25% PFA (total solid weight) to treat As and Pb contaminated soils by S/S, the pH levels were 5.5 - 6.5. Ciccu et al[2003] reported that a small amount of PFA in the ratio 10: 0.75 ratio of soil: PFA reduced the leaching rate of heavy metals, below the regulation limit.

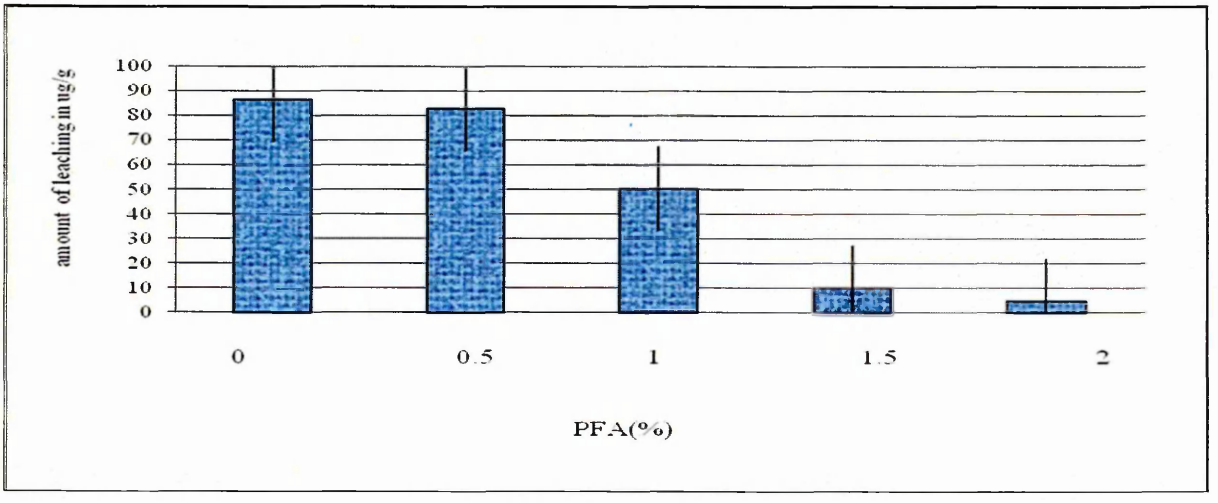

Figure 7. 2 Effect of adding different concentrations of PFA to lead-contaminated soil (n=3)

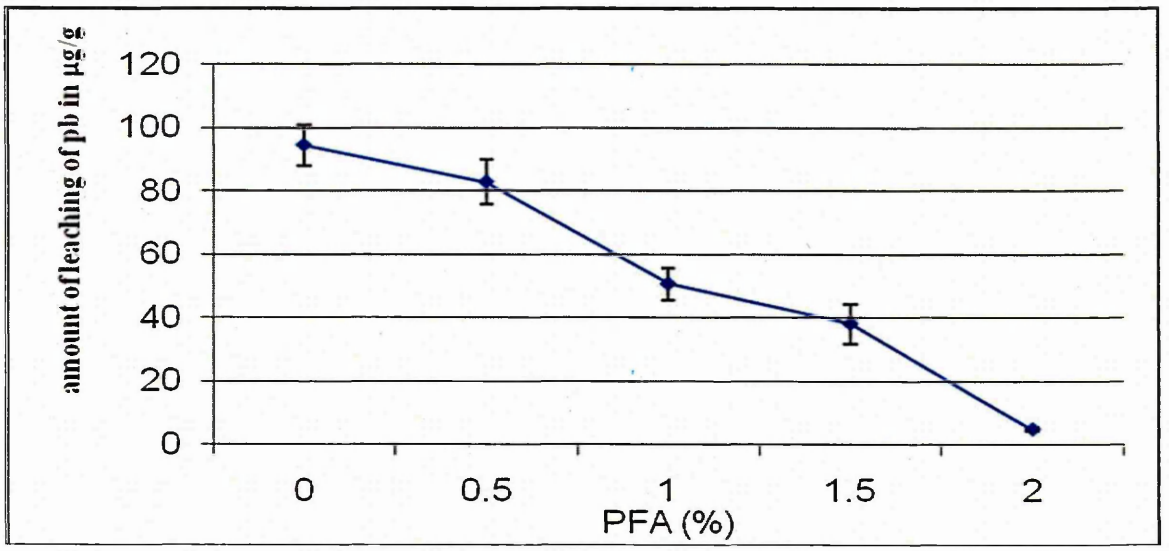

Figure 7.3 Effect of adding different concentrations of PFA to lead-contaminated soil , followed by leaching with 50 ml of deionised water (n=3)

Dermatas and Meng [2003] have reported than when the pH < 9, the Pb release while it is still influenced by surface adsorption, is mainly solubility controlled. In this study, which uses PFA only to stabilize lead contaminated soil, the pH of the final solution was 6.5. Also they reported that more specifically, fly ash addition results in further increase in the pH range of Pb immobilization from 5 to 13. Kumpien et al [2007] are in agreement with this pH value for samples treated with PFA, so it was concluded that the adsorption capacity of PFA and pH independence are the main reason for the reduction of Pb in the final leaching solution, which refers to the amount of silicon dioxide (SiO_2), calcium oxide, aluminium oxide (Al_2O_3) and iron oxide (Fe_2O_3) present in the PFA. After treating soil with PFA increasing amount the Ca and Na concentrations decreased rapidly Mg concentration also decreased, (see Table 7. 5 and Table 7. 6). Zhang et al[2009] in agreement with the trend of this results and also Cl- and SO_4^{2-} concentrations for treated soils significantly increased (see Table7. 6 and 7.7). Shao et al [2009] have reported that zeolite can lead to the immobilization of metals in three ways. Firstly, when zeolites dissolve they raise the pH level of acid polluted soils causing the precipitation of insoluble phases which contain metals. Secondly, the increase in alkalinity promotes a negative charge on mineral surfaces due to deprotonation of the surface unsaturated bonds. Increasing the pH value increases the cations and natural zeolite, especially, plays a significant role in surface complexation because of its high specific surface, thirdly, metal retention may also take place regardless of pH value due to the cation exchange in zeolit Kumar and Sharma[2004] have reported that addition of PFA

to soils will affect the plasticity, hydraulic conductivity and swelling properties of the blended cement decreased and the dry unit weight and strength increased with an increase in fly ash content.

Table 7.4 Effect of 0.1g of fly ash on lead contaminated soils leached with deionised water.

Sample	Leaching of Pb in final solution mg/l	Leaching of Pb in final solution(µg/g)	pH
5g of Pb Contaminated. Soil +50 ml Deionised water	8.2	82.0	4.61
5g of Pb Contaminated. Soil +50 ml Deionised water	7.8	78.0	4.58
5g of Pb Contaminated. Soil +50 ml Deionised water	8.0	80.2	4.59
Mean	8.0	80.7	4.59
sd	0.2	2.00	0.015
5g of Pb Contaminated. Soil +50 ml Deionised water + 0.1g of PFA	0.37	3.74	5.96
5g of Pb Contaminated. Soil +50 ml Deionised water + 0.1g of PFA	0.27	2.77	5.96
5g of Pb Contaminated. Soil +50 ml Deionised water + 0.1g of PFA	0.23	2.28	6.20
Mean	0.29	2.90	5.97
sd	0.07	0.74	0.13
5 g of uncontaminated soil + 50 ml of Deionised water	0.054	0.55	5.09
l5g of uncontaminated soil + 50 ml of Di water	0.095	0.95	4.95
5g of uncontaminated soil + 50 ml of Deionised water	0.048	0.49	5.20
Mean	0.06	0.66	5.1
sd	0.02	0.25	0.12

Table 7.5 Effect of PFA on lead contaminated soils and subsequent release of other elements

sample	Pb (µg/g)	Mg (µg/g)	Ca (µg/g)	Na (µg/g)	K (µg/g)	pH
Pb contaminated soil + Deionised water	34.0	22.3	140.7	ND	13	4.95
Pb contaminated soil + Deionised water	33.5	17.1	136.8	ND	17.2	5.54
Pb contaminated soil + Deionised water	39.0	15.3	129.9	ND	23	5.66
Mean	36.1	17.9	139.4	ND	14.4	5.2
Sd	3.1	3.06	22		2.06	
Pb contaminated soil + acid wash	610.2	NM	NM	NM	NM	
Pb contaminated soil + acid wash	580.3	NM	NM	NM	NM	
Pb contaminated soil + acid wash	585.4	NM	NM	NM	NM	
Mean	595.1	NM	NM	NM	NM	
Pb contaminated soil+ 0.1g of PFA + Deionised water	ND	17.1	188.7	15.1	19.3	6.21
Pb contaminated soil+ 0.1g of PFA+ Deionised water	ND	15	176.1	14.1	25.5	6.28
Pb contaminated soil + 0.1g of PFA+ Deionised water	ND	15.4	176.4	13.4	18.2	6.07
Mean		15.8	180.4	14.2	21	6.18
Sd		1.1	7.18	0.85	3.93	0.1
acid wash						
Pb contaminated soil + 0.1 g of PFA+acid wash	550.2	NM	NM	NM	NM	
Pb contaminated soil+ 0.1g of PFA+acid wash	546.8	NM	NM	NM	NM	
Pb contaminated soil+ 0.1g of PFA+acid wash	590.3	NM	NM	NM	NM	
Mean	562.2					
Sd	24.07					

ND = none detected, NM=not measured

7.2.4 The Effect of Type of Leaching Fluid

The effect of leaching fluids with different pH values was investigated using HNO_3 at various concentrations. At low pH (1.2) maximum extraction was achieved for Pb and the associated elements Ca, Mg and Na, (see Table 7.6). 5g of soil and 0.1 g of PFA were mixed together with 50ml of leaching fluid. The maximum extraction was 858 µg/g by using 0.1M HNO_3.

Table 7. 6 Effect of PFA on release of lead with three leaching fluids and consequent release of Ca , Mg , Na and K

Sample	Leaching fluid	pH	Pb (µg/g)	Ca (µg/g)	Mg (µg/g)	Na (µg/g	K (µg/g)
5g of Pb contaminated soil	50ml D.I water	5.4	37.6	140	19	5.4	17
0.1g of PFA + 5g Pb contaminated soil		6.2	0	180	17	14.1	21
5g of Pb contaminated soil	50ml 0.01M HNO_3	2.2	744	2400	270	4.0	19.6
0.1g of PFA + 5g of Pb contaminated soil			622	2800	370	29	29
5g Pb contaminated soil	50ml 0.1M HNO_3	1.2	858	2600	280	5.0	22.1
0.1g of PFA + 5g of Pb contaminated soil			786	3500	330	23.8	41

The effect of adding PFA was a reduction in Pb released to an undetectable level at higher pH levels. At the lower pH levels (2.2 and 1.2) for the leaching fluid the reductions were only 8% and 5% respectively. PFA can only effective, stabilize material with higher pH leaching fluid such as DI water which has a pH value of 5.6. (see Table 7.6). Orhan et al,[1999] in agreement with this result and reported that a low pH value (2.5 ±3), the hydrogen ions compete with heavy metal cations and the percentage removal of metals decline. At intermediate pH values (3 ±6), the degree of removal mainly depends on the ionic size of the metal. Above pH 6, precipitation becomes dominant especially for Pb_2ions.

Kim et.al [2006] carried out a investigation of formatted compounds as a result of adding PFA and adjusting the pH and concluded that the sample set was divided into alkaline and acidic samples based on the ability of the ash to buffer the pH of the acid leachants.

Anhydrite was identified in the alkaline samples, while gypsum was the $CaSO_4$ mineral identified in the acidic samples.

Kumpiene et al[2008]found that Ca compounds were generally efficient for Pb immobilization, which is mainly due to an increase in soil pH. Since the soil pH might not be stable and acidification would lead to Pb release, application of Ca compounds alone might not be sufficient for a long-term Pb immobilization.

Alkaline compounds are more useful if used as supplements to neutralize soil acidity caused by other compunds, e.g. phosphoric acid. Highly alkaline conditions can have a reverse effect on Pb stability due to the amphoteric nature of Pb, and at pH > 11–12 formation of soluble Hydroxide complexes can increase Pb mobility [van der Sloot et al., 1997; Garcia et al., 2004]. However, such high pH values are unusual for soils. Application of 1% lime to ten contaminated soils showed no significant effect on the acid extractable Pb fraction or increased the Pb leaching. [Inga et al 2009].

According to Peng et al [2009] the pH value is a key parameter controlling heavy metal transfer behaviour in sediment. Normally, with pH decreasing in sediment, the competition between H+ and the dissolved metals for ligands (e.g. OH^-, CO_3^{2-}, SO_4^{2-}, Cl^-, S^{2-} and phosphates) becomes more and more important. It subsequently decreases the adsorption abilities and bioavailability of the metals, and then increases the mobility of heavy metals. Sometimes, with a small change in pH level, the percentage fixation of heavy metals on sediment particles may range from almost a 100% to none .According to Tingle et al.[1993] soils with pH < 4 do not have surface-bound Pb, whereas soils with pH > 4 do. With pH = 2.0 there was no detectable surface-bound Pb, and they concluded that with increasing pH, the amount of Pb adsorbed on surfaces increases due to the increasing negatively charged character of most mineral surfaces.

7.2.5 The effect of adding PFA to soil contaminated with Pb, Zn, Ni , Cd, Cr, and Cu

Table 7.7 shows the effect of the addition of PFA to soil contaminated with a 1000 mg/l solution of a mixture of heavy metals (Pb, Zn, Ni, Cd, Cr, Cu) in DI water see Chapter two for details of the contamination process. The leaching batch tests were conducted for 2 hours on the platform shaker. The S/L ratio was 1:10 and the leaching fluid was 50ml of DI water. The treated soils had an average pH of 5.0 and the concentration of lead was detectable and a

noticeable reduction in the amount lead in the leachant was recorded, down from 884μg/g to 377μg/g, and Zn was reduced from 963 to 549 μg/g, Ni from 1079 to 604μg/g, and Cr from 905 to336 μg/g, etc (see Table 7.7).

Table 7.7. The effect of 0.1g PFA on 5g of soil contaminated with 1000ml of solution containing 1000mg/l of Pb, Zn, Ni, Cd, Cr and Cu, leached with 50ml of DI water

Sample	Pb (μg/g)	Zn μg/g)	Ni (μg/g)	Cd (μg/g)	Cr (μg/g)	Cu (μg/g)	Cl^- (μg/g)	NO_3^- (μg/g)	SO_4^{2-} (μg/g)	pH
Mix metal contaminated soil +DI water	857	880	905	987	881	927	17.1	18890	20.7	4.1
Mix metal contaminated soil +DI water	883	1065	1084	1193	902	1107	17	18750	33.7	4.0
Mix metal contaminated soil +DI water	912.3	946.4	975	1056	933	979.7	11.2	16370	30.01	3.9
Mean	884.1	963.8	988	1079	905.3	1005	15.1	18003.2	28.14	4.0
Sd	27.7	93.7	90.2	104.9	26.2	92.5	3.3	10208	6.7	0.07
Mix metal contaminated soil + 0.1g PFA	323.7	570.2	624.9	811.5	335.1	754.9	14.69	11480	96.82	5.4
Mix metal contaminated soil + 0.1g of PFA	281.5	473	510.8	665.9	287.2	607.2	13.98	9006	145.9	4.9
Mix metal contaminated soil + 0.1g of PFA	375	605.1	679	925.9	387.1	865.9	12.50	13350	133.3	4.7
Mean	326.7	549.4	604.9	801.1	336.4	742.6	13.7	11280	125.3	5.0
Sd	46.82	68.45	85.8	130.3	49.96	129.7	1.11	2180	25.51	0.3

Table 7.7 clearly shows that addition of PFA substantially reduced the leaching of metals in contaminated soils, generally by a factor of between one third about (Cd, 25.7%) and two-thirds (Cr 62%,), as detected by ICP(AES) technique. Addition of PFA reduced the average release of SO_4^{2-} and NO_3^-, but results were not as clear for Cl^- because of the large standard deviation associated with the readings. The large amount of NO_3^- released was due to presence of NO_3^- in the contaminated soil.

Table 7.7 shows that the average concentration of Pb released from the contaminated soil and leached out with DI water, in the presence of other contaminating metals, was 884μg/g. That is the amount of lead released in the presence of other contaminating metals was higher than when it was on its own, 884μg/g compared to 39μg/g. Wobst et al[2001] in support of this behaviour of lead reported different discharge of single element than mixtures of metals which was influenced by the presence of other heavy metal oxides. Also Namasivayam and

Ranganathan [1995] agreed with this difference and attributed this to two different factors, ionic radius of the metals and the hydrolysis constant of metal ion.

In this study, the high reductions were for Pb and Cr about 57%, Cr 62%, respectively, followed by Zn about 42 %, then Cu equal 26%, and Cd 25.7%, (see Table 7.7).

7.2.6 The acid digestion test for mixture of metal contaminated soils

For the procedure see chapter two. section 2.2.4 The maximum extractions of Pb, Cd, Cr, Cu, Ni and Zn were obtained for 1g of contaminated soil using the total digestion acid test with 5ml of HNO_3 and 25ml of DI water on a hotplate for 10min, and filtered with Whatman 543 ashless filters and results are shown in chapter three. Fig. 3.4.

7.3 Characterisation of precipitated materials

Further investigation was required to explain the chemical reactions which occurred during the leaching tests and with contact between the stabilized materials and contaminants either in solution or the soils. The most used chemical analytical tools in this field are Fourier Transform Infrared (FTIR) , Raman spectroscopy, X-ray diffraction (XRD) and X-ray Photo Spectroscopy (XPS).

7.3.1 Fourier Transformation Infrared Spectroscopy

The FTIR was used for qualitative analysis to the investigate the relationship between the lead contaminated soil and solution and stabilized material. The samples were prepared as described in Chapter 3, Section 3.5.2. In Figure 7.4 the B-spectrum of contaminated soils with PFA added shows peaks at 1225 and 1625cm^{-1} and troughs in the 3000-3350cm^{-1} region, both of which refer to the samples after treatment with PFA to stabilize the lead contaminated soil. As can be seen these are the major differences from the spectrum of the untreated, contaminated samples. according to Barnett et al [2002] the peak 3346 cm^{-1} is assigned to symmetric and asymmetric stretching (Vl and V3 of O-H), see chapter 6 Table 6.11, which can be attributed to either PbOH or PbO. Deformation (V2)H_O_H at 2088 cm^{-1} and 1625 cm^{-1},1362cm^{-1} which are assigned to V3.CO_3^{2-} can be attributed to $PbCO_3$ which is in agreement with ESEM, XPS results in this study, it is possible to form PbO or PbOH since the pH in final solution was 6.2.

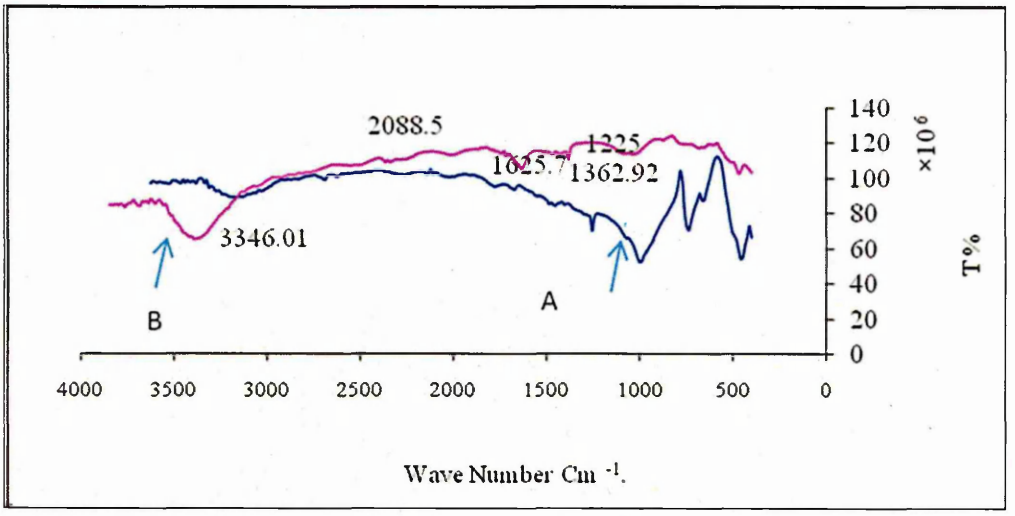

Figure 7.4 FTIR spectra: (A) , lead contaminated soils, (B) lead contaminated soils treated with 0.1g of PFA leached with 50 ml of deionised water

7.3.2 Raman spectroscopy investigation

In a similar analysis, Kirkpatrick et al., (1997) found peaks at 462cm^{-1} which they attributed to internal deformations of Si-O (O-Si-O bending) between 430-540cm^{-1}. It is obvious that here there is a major peak in all three spectra at just 462cm^{-1} and it is believed that this is also due to internal deformations of Si-O. See Fig. 7.5 results of this study. Apart from the dominant peak just under 500cm^{-1}, there is only one other clear peak visible. This is at 1040-1100cm^{-1} for lead contaminated soil, but which the Raman database attributes to calcite. According to Guillaume et al., [2007] this can be assigned to $V_3(SO_4)^{2-}$ which shows the formation of lead in soils attributed to $PbSO_4$. This is in agreement with results obtained by FTIR and XRD for lead contaminated soil, see Chapters 3 and 4. It is noted that the Raman technique is not sufficiently powerful to identify the effect of GGBFS on soils as compared with other techniques used in this study, e.g. FTIR, XRD and XPS.

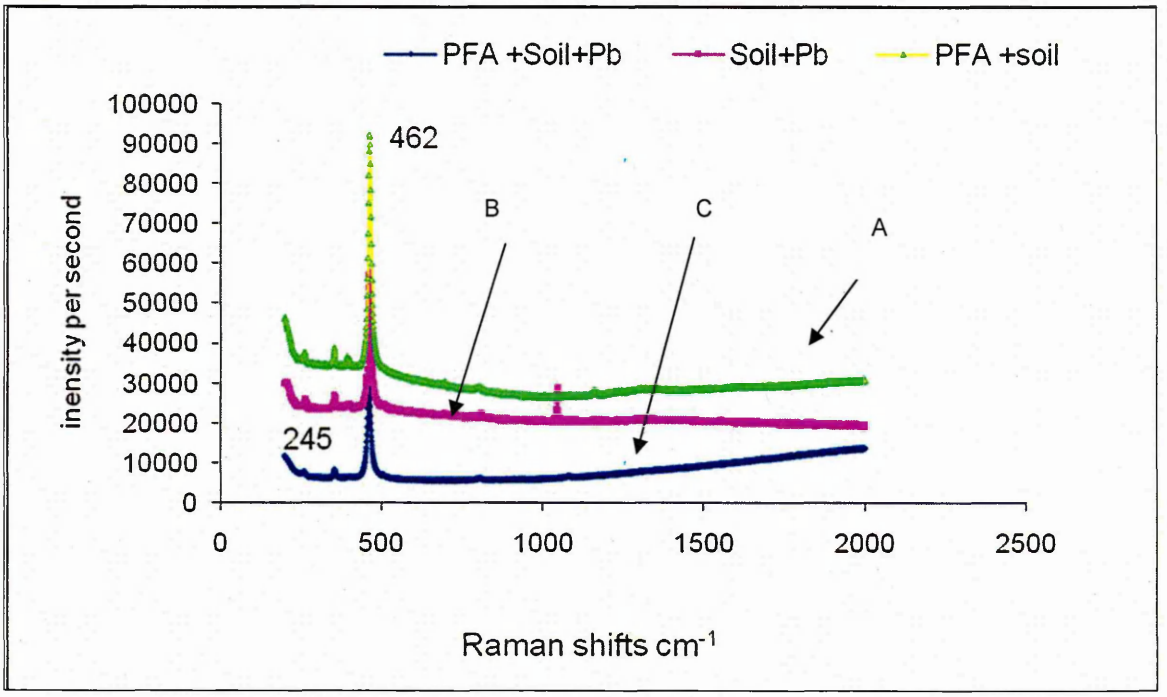

Figure 7.5 Raman spectra for: (A) uncontaminated soil mixed with 0.1g PFA,(B)-soil contaminated with 20,000mg/l of lead, (C)- as B but treated with 0.1 g of PFA

7.3.3 X-ray diffraction investigation (XRD)

X-ray diffraction analysis (XRD) was used to investigate a 20, 000mg/l Pb solution stabilised by GGBFS. The 20,000mg/l strength solution was used to enable XRD (and other techniques) to characterize and measure the Pb in the sample. The suggestion from the leaching test analysis using the ICP (AES) technique to measure concentration of lead in the final solution, indication no lead in the leachat, that the formation of lead on the surface of the PFA is partly by precipitation as a result of increase in the pH of the final leaching solution, and also by the absorption of lead on the surface of the PFA. The latter is confirmed by the Environmental Scanning Electron Microscope (ESEM), see below, which shows the lead on surface of the PFA In addition the acid wash on the surface of the filter funnel and the ICP(AES) measurement of the concentration proved that lead is being mobilized by PFA, see Tables 7.5.Rha et al [2000] used ICP, ESEM and XRD techniques to investigate the efficiency with which PFA stabilised heavy metals using similar techniques to those used in this study, and reported similar results on the efficiency of PFA as a stabilizer material.

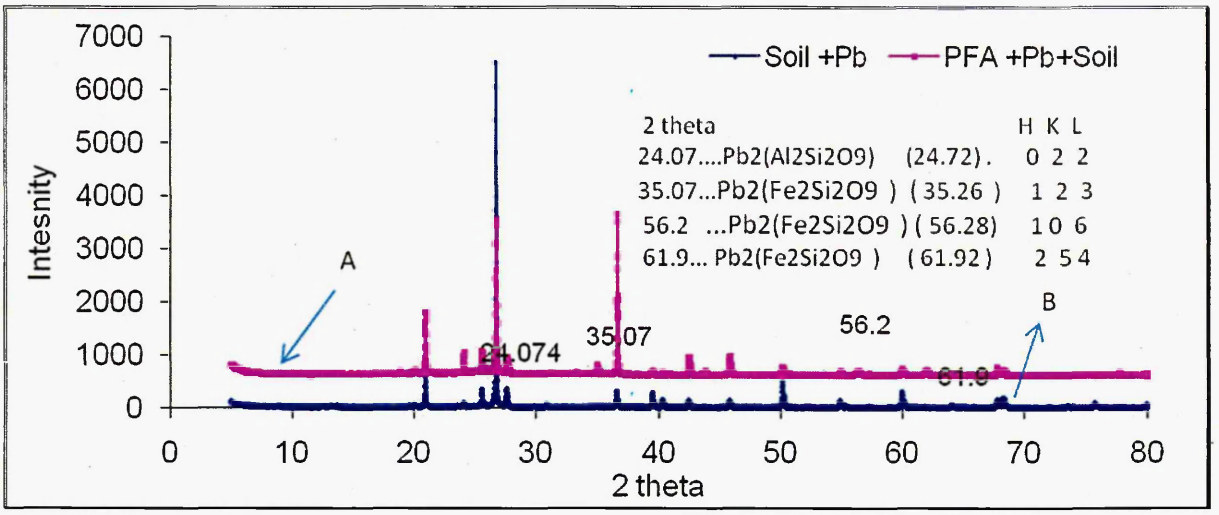

Figure 7. 6XRD investigation for soil contaminated with Pb and contaminated soil after treatment with PFA; A-line, spectrum for contaminated soil treated with PFA, and B-line, spectrum for lead contaminated soil

In regard to the Cambridge XRD database [http://www.cds.dl.ac.uk] and according to Dorsam et al [2008] who reported the formation of $Pb_2(Al_2Si_2O_9)$ on the surface of PFA and the formation of melanotekite-$Pb_2(Fe_2Si_2O_9)$-[PBCN] at 56.3 theta, which is also in agreement with the results obtained in this work. See Fig.7. 6, the PBCN is the number of the dimensions in the space group of crystal.

7.3.4 Environmental scanning electron microscope (ESEM)

Many researchers for example, Diamond (2004) and Rha. et al. (2000) have concluded that no other technique can provide the same depth and breadth of information, in particular with use of the backscatter-mode, as ESEM. Figure 7.7a, shows the precipitated lead on the surface of PFA particles used to treat lead contaminated soils. Energy dispersive X-ray analysis (EDX) of the PFA stabilized Pb contaminated soils, Figure 7.7b confirms that lead is present in the sample, but there is no indication of the spherical shape of the lead which can be seen in Figure 7.7a.Taube et al [2008] have reported the spherical shape of lead in cementitious material, and this is often referred to as lead being adsorbed and incorporated into elements such as C, Si, Fe, Mg, or Al within the PFA, which is in agreement with results obtained by XRF in this study see Table 7.1, also the ESEM proved the Pb was mobilized by PFA in Fig 7.8a the untreated soils and EDX analysis of spectrum 1 in Fig.7. 8b

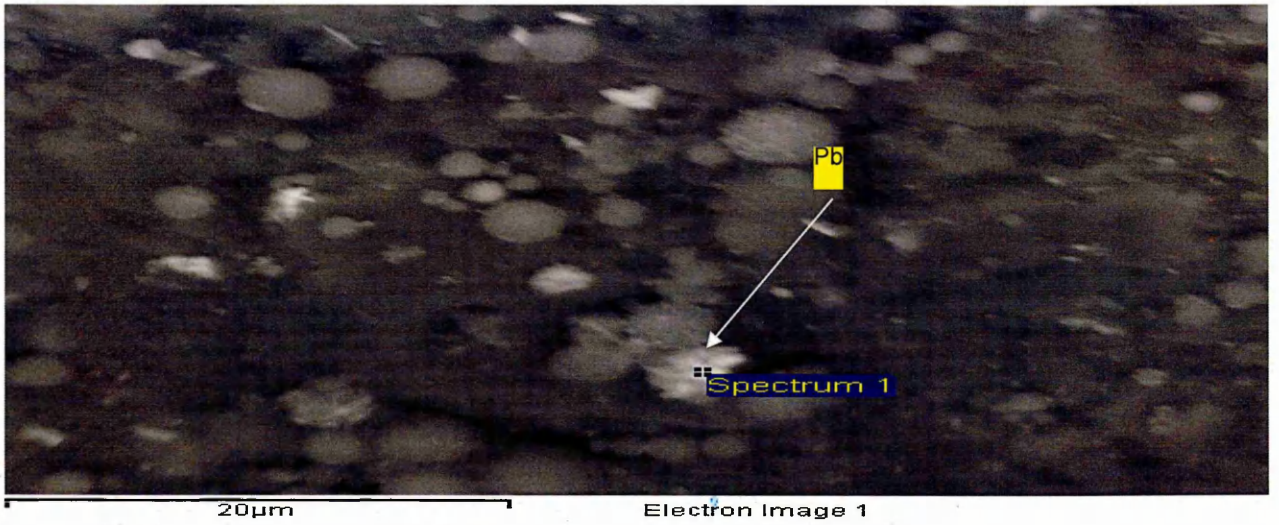

Figure 7.7a Environmental scanning electron microscope: lead contaminated soil and lead contaminated soil treated with 0.1g of powdered PFA

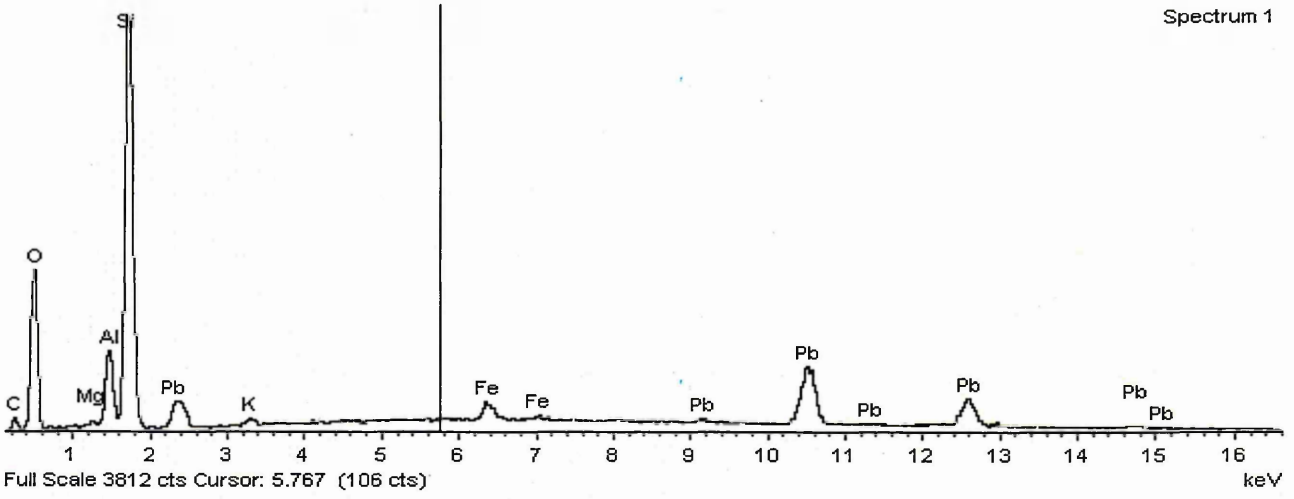

Figure 7.7b Energy dispersive X-ray analysis of 5g of soil contaminated with 50ml of lead solution of strength 20,000mg/l treated with 0.1 g of powdered PFA

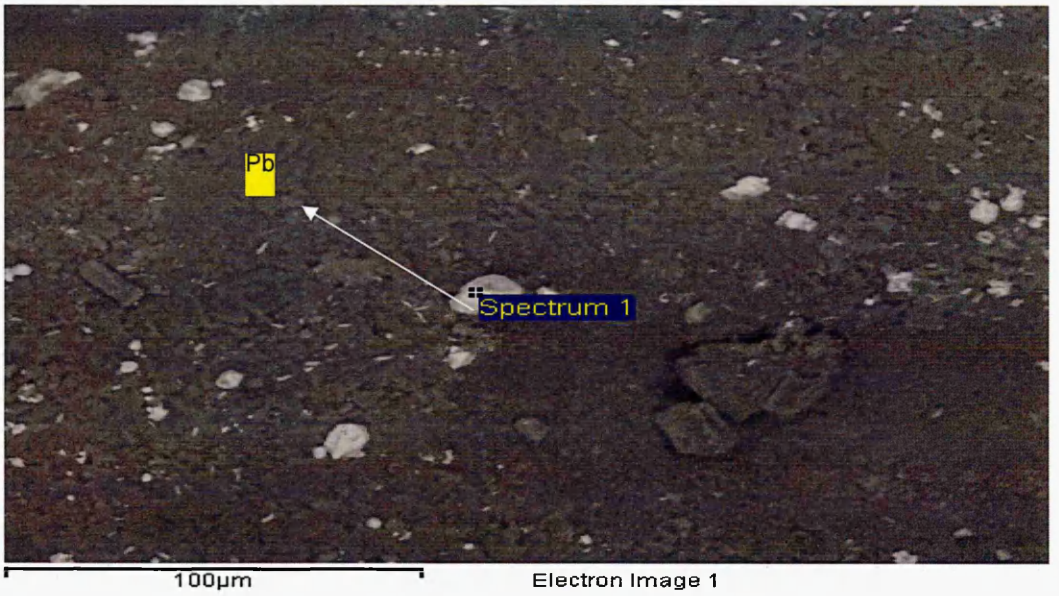

Figure 7.8a ESEM image Pb contaminated soil Pb at spectrum 1

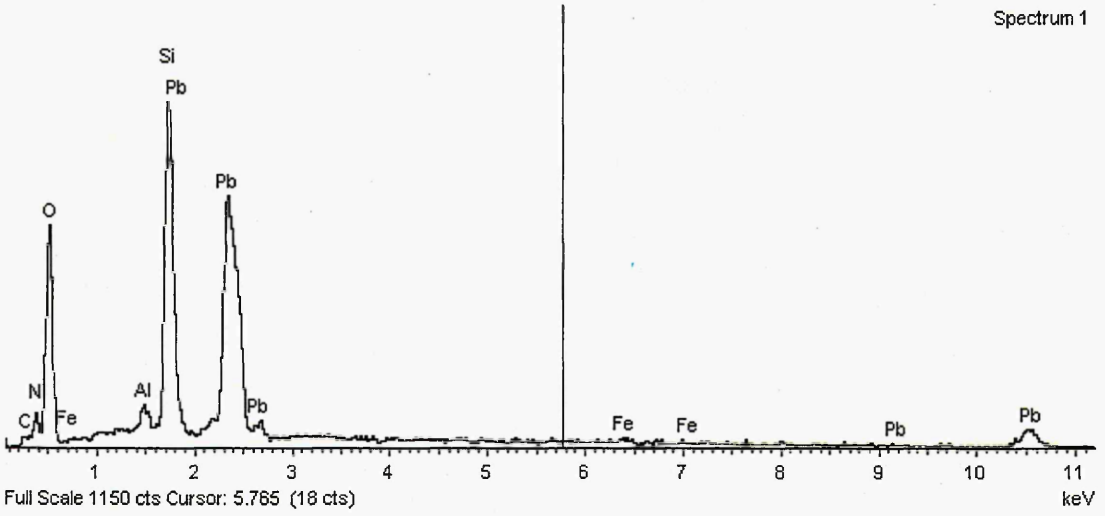

Figure 7.8b EDX map for ESEM image at spectrum 1 for Pb contaminated soil element present include (Pb, Al, Si, Fe, O, C, and C)

7.3.5 X-ray photoelectron spectroscopy

7.3.5.1 XPS investigation of lead contaminated soil

Figure 7.9 presents a wide scan of untreated lead contaminated soil. It clearly shows a peak at 136eV due to lead Pb4f. The most common elements were O1s, Si2p, and Al2p, which account for about 56%, 20% and 8%, respectively, while Ca2p accounts for just 1%. See also Figures 7.9 and 7.10. According to the XPS international data base the peak at 136eV is assigned to Pb4f7 and the peak at 141eV is assigned to Pb4f5. Classifying those peaks (see also James et al, [2008]) the peaks at 136eV and the doublet at 141eV are assigned to PbO and $PbSO_3$.

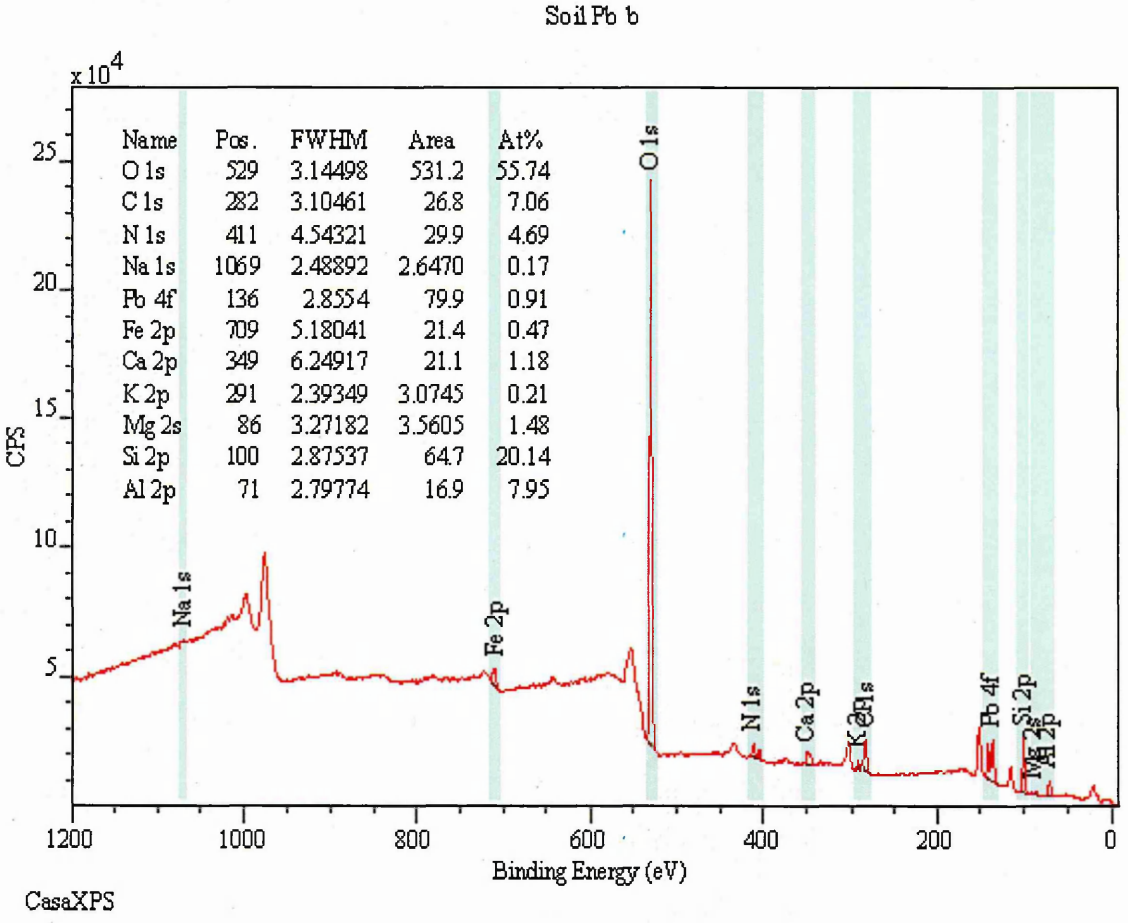

Figure 7. 9 Wide scan X-ray Photoelectron Spectroscopy analysis of 5g of soil contaminated with 50ml lead solution of strength 20, 000mg/l

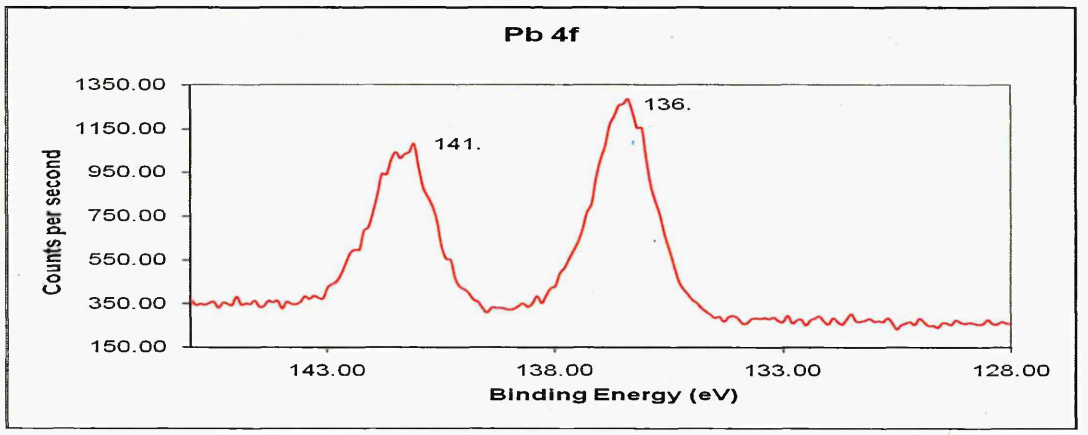

Figure 7.10 Detailed X-ray Photoelectron Spectroscopy analysis of 5g of soil contaminated by 50ml of lead solution of strength of 20, 000mg/l in the region of the lead 4f spectral peaks

7.3.5.2 XPS Lead contaminated soil treated by PFA

In sample treated by PFA, the lead formed as Pb4f which accounts for about 2,07 % of samples while O occupied 50% and 16.8 % is Si2p.(see Fig.7.11). The Ca2p occupied only 0.80 % less than untreated samples (see Fig7.10) which can be attributed to the reaction of Ca and O with Pb, that may lead to formation of lead carbonate ($PbCaO_3$) on surface of samples or PbSiO. XRD described in results section 7.6.3 and ESEM in 7.6.4.1 are in agreement with the results. As a result of adding PFA to lead contaminated soils, the Si2p decreased to 50.2% in area and to 16.2% , from 64% area and 20.4% (see Fig,7.9) ,lead contaminated soils and Fig 7.11 for PFA treated soil, also there was a slight increase in Fe2p area to 223, 0.53 % . There was no detection of Na1s in PFA treated samples. The classification of lead at 141.1 and 136 .5 eV in Figure 7.12 are assigned to Pb4f7/21 which is according to James et al, [2008], $PbSO_3$ or Pb SO_4 . The peak centred at 137.5 eV is assigned to lead oxide species (i.e., PbO and/or PbO_2) .Tauson [2009] supports this result. In addition in Fig 7.13 are the peaks distribution for Pb4f, the major peaks are assigned to Pb4f 7/21 with 137.99 eV, followed by Pb4f7/22 with 139.5 eV, under this Pb4f7/2 1 range of 136.5 to 141.1 eV. Its attributed to be Pb-S group, although there is no peak to suggest presence of $PbCO_3$,but this is assigned according to Tingle et al [1993]. The Pb 4f7/2 binding energy in $PbCO_3$ is 138.3 eV, slightly above that measured in these soils,(see Fig,7.11) confirming that carbonate species are present on some surfaces (spectrum not shown). Thus, $PbCO_3$ species may also be present. However according to Fig 7.13, a multi-compound has been formed on the surface such as Pb4f7.21, Pb4f7/22, Pb4f5/22 and Pb4f5/21 which they are refereed to PbO or PbOH and Pb-S_x .Casella [2001] in support of this conclusion .

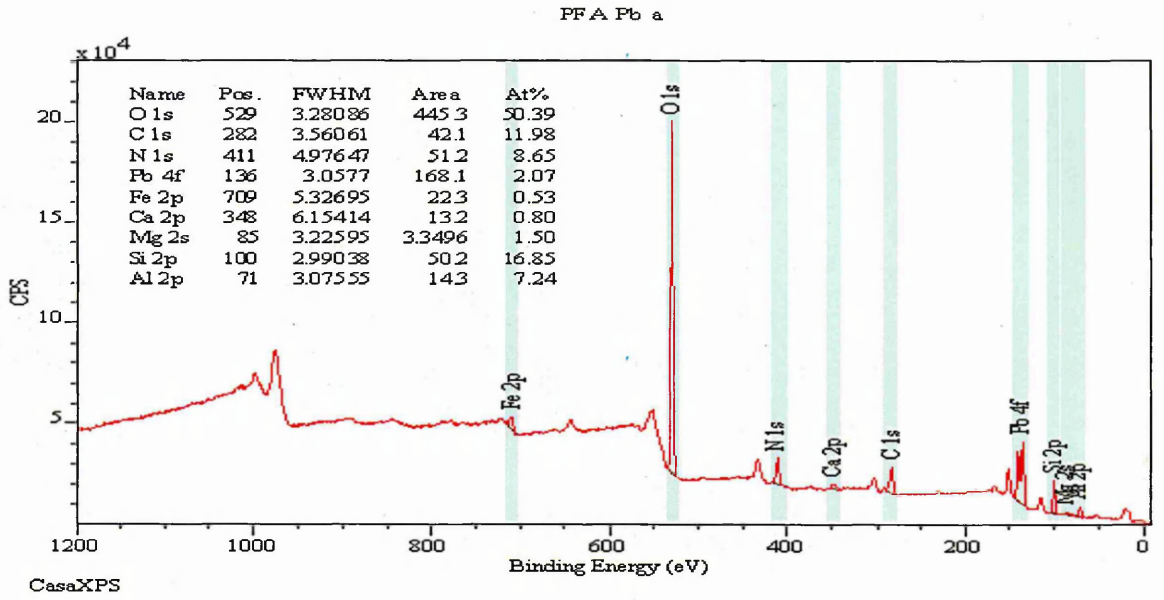

Figure 7. 11 Wide scan X-ray Photoelectron Spectroscopy analysis of 5g of soil contaminated with 50ml lead solution, of strength 20,000mg/l, stabilised by 0.1 g PFA

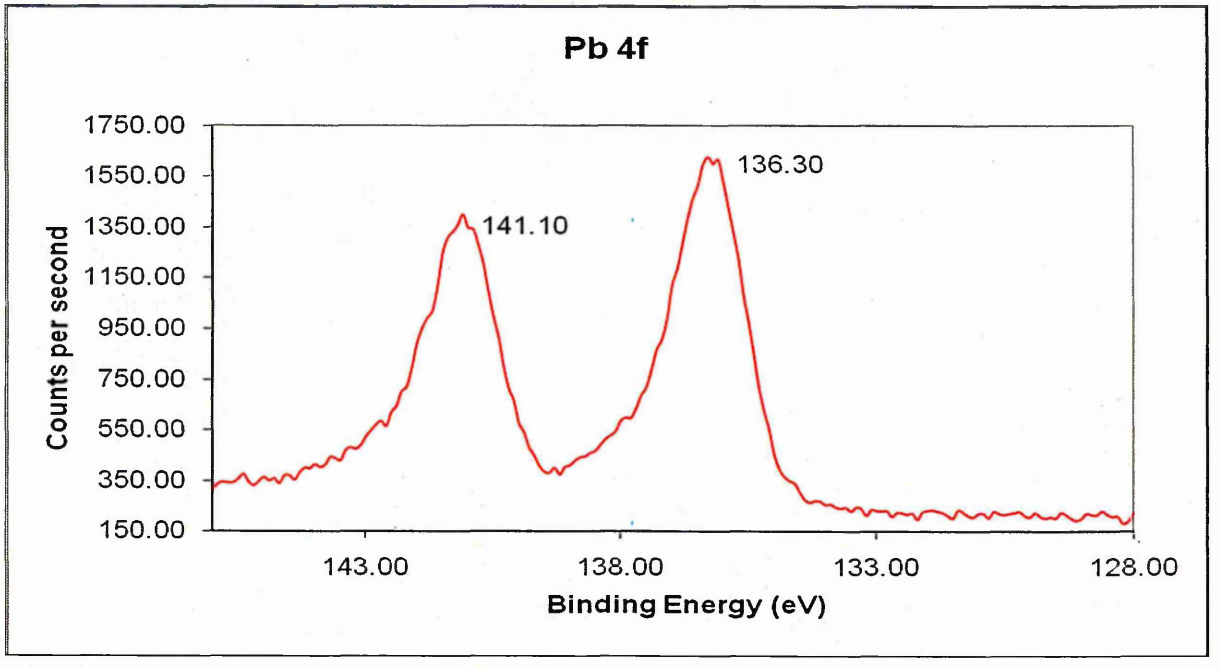

Figure 7.12 Detailed XPS analysis of the spectrum for lead contaminated soil treated with PFA, for the region of the lead 4f spectral line

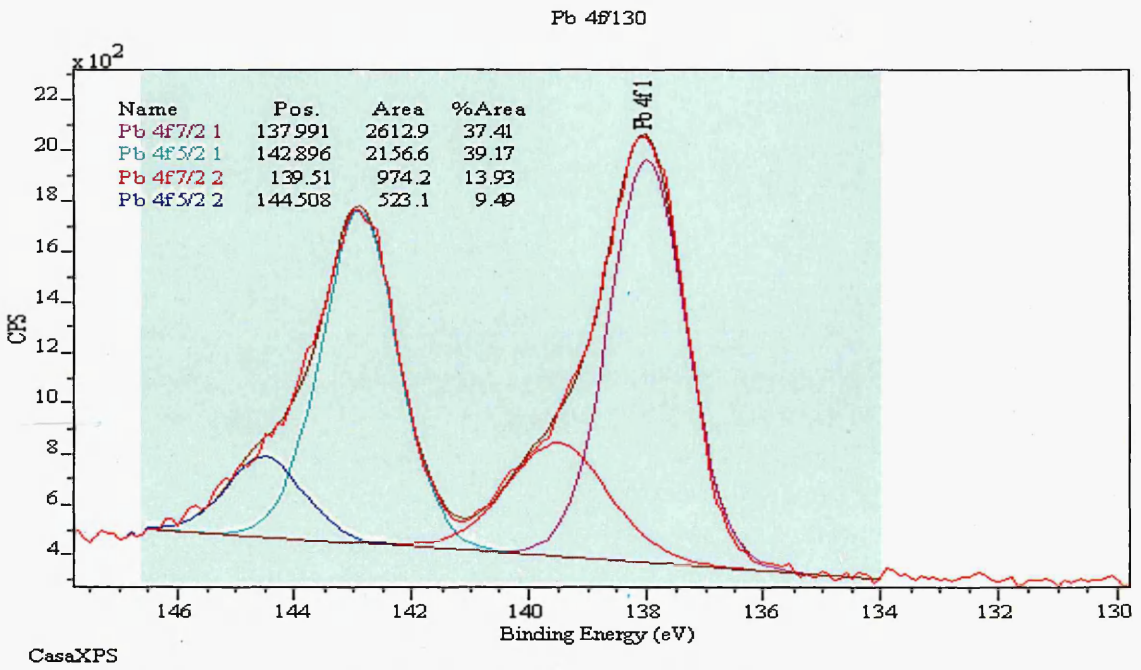

Figure 7.13 Distribution of lead peaks by XPS analysis of the spectrum for lead contaminated soil treated with PFA, for the region of the lead 4f spectral line

7.4 The effect of using coal fly ash to replace OPC

Coal fly ash (typical diameter range 0.1μm to 0.1mm, with an average of 15μm) is generally finer than Portland cement (1-l00 mm). Its main constituents are silica, alumina, and various oxides of calcium and iron. Its physical and chemical properties depend on the quality of the coal used, the degree of coal pulverization, flame temperature, oxidation conditions and system of collecting and storing of the fly ash. (See Table 7.1) for the properties of the PFA used in this study.

Pozzolanic materials are also used either separately or as an admixture with PFA for S/S purposes. The mineralogical composition and the relative proportion of various oxides in pozzolans are different from those present in Portland cement. They contain SiO_2, $A1_2O_3$, Fe_2O_3 and a small amount of CaO, they are rich in SiO_2 and poor in CaO, while the reverse is true for dry clinker in cement.[Kaur 2005]

Pozzolanic substances alone are not cementitious, but they may become so if allowed to react with lime and water. When blended pozzolanic cement is hydrated, the clinker compounds react first to produce, among other things, lime. Subsequently, the reactive oxides such as SiO_2, $A1_2O_3$ and Fe_2O_3, in the pozzolans react with this lime to produce mainly calcium-aluminate-hydrate (CaO-A1$_2$O3-H_2O), calcium-aluminate-silicate-hydrate (CaO-A1$_2$Oa-SiO_2-H_2O), calcium-alumino-ferrohydrates (CaO-Al_2O_3-Fe_2O_3-n2O) and calcium-silicate-

hydrate ($CaO-SiOE-H_2O$) phases. These phases have similarities with those obtained after hydration of ordinary Portland cement Yousuf et al [1995].

International Standard ASTM C618 (Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use as a Mineral Admixture in Concrete) defines two classes of fly ash; Class C and Class F, to reflects the differences in their pozzolanic and cementitious properties. Class C fly ash is produced from the combustion of sub-bituminous coal or lignite and contains between 15 to 30% lime, while Class F fly ash is usually produced from the combustion of anthracite or bituminous coal and contains less than 7% lime, but contains more alumina, iron and silica oxides. Its chemical composition suggests possible applications for coal ash as a replacement material for OPC.

Reactive silica and free lime contents are necessary for pozzolanic reactions to take place. Sarat and Yudhbir [2006] have also observed that the amount of SiO_2 or $SiO_2 + Al_2O_3$ in fly ash influences the pozzolonic activity. Pandian [2004] has reported that the presence of a relatively high percentage of carbon in the fly ash decreases the pozzolonic activity and that the compressive strength of fly ash generally improves with time due to pozzolanic reactions.

The C-S-H produced in the pozzolanic reaction has a lower density than that formed from Portland cement hydration. However, since the reaction is much slower, the products of the pozzolanic reaction fill the already existing capillary spaces in the cement paste; thus, it improves strength properties and reduces permeability [Alhozaimy et al., 1996].

Qian et al [2008] showed that the combination of calcium sulpho-aluminate (CSA) cement with MSW fly ash was interesting for three reasons: (i) CSA cement is an ettringite cement with a number of qualities superior to those of OPC – quick hardening and high initial strength, resistant to both corrosion and frost, and high impermeability; (ii) Because MSW fly ash tends to be rich in sulphur and chlorine it can react relatively easily with, for example, calcium sulpho-aluminate to form an ettringite–Friedel matrix; (iii) the formation of such a matrix would favour the durability of GFRC composites because it would keep the alkalinity of CSA-MSW fly ash system lower.

C-S-H comprises about 60% of hydrated cement volume and it is the most important hydration product that provides strength and bond to the cement paste.[Neville, 1996; Pan., et al 2007; Safiuddin et al. 2007]. The other major component of hydrated cement is $Ca(OH)_2$ which forms 20% of hydrated cement volume but it does not itself contribute to its strength.

$Ca(OH)_2$ can react with siliceous and aluminous materials in fly ash to form strong and durable cementing compounds, no different than those formed during hydration of OPC. This reaction can be shown as:

Calcium silicate + fly ash +water---- durable binder-----calcium silicate hydrate

$$C_3S\ C_2S\ +H_2O \text{ ------ } Ca(HO)_2 + \text{fly ash} + (C\text{-}S\text{-}H)$$

Recently Meyer [2009] has listed a number of advantages of adding fly ash to concrete, including: lowering of the cost, improved workability and higher long-term strength, significantly improved resistance to sulphate attack and alkali-silica reactions, improved permeability, lower porosity and shrinkage characteristics and lower heat of hydration.

Previous authors [Liu and Beaudon, 2000; Hassan et al 2008] have noted that the main disadvantages of fly ash are: increased risk of frost damage in the freeze-thaw cycle because the high carbon content in some fly ash causes air entrainment; the curing process was much more important than for OPC and took significantly longer to attain the required strength, the addition of fly ash to concrete results in a finer pore structure, in both the cement paste matrix and the paste-aggregate interface.

7.4.1 The effect on leaching of adding fly ash to OPC to stabilize Pb

The effects of adding different amounts of fly ash to the dry OPC powder were observed. The %PFA was calculated on the total dry weight so, for 30% PFA, 200g of dry powder was composed of 140g OPC and 60g PFA. Three series of tests were carried out: using 10%, 20% and 30% PFA. The mixing of the two dry powders took place prior to introducing the contaminant solution. The mix was in the ratio 0.4:1 water/cement, it was then cured in the mould for 7 days, after which time it was solid and in the shape of a cube suitable for the leaching test, for details see Chapter 2. Asavapisit et al [2005] also used 0 %, 10%, 20% and 30% PFA in a PFA/OPC mix.

Berryman et al [2005] reported that he used 35% PFA to reinforce concrete OPC pipes because 35% is the limit set by the American Society for Testing and Materials (ASTM). Singh et al [1990] used a mix where PFA was 25% of the total weight. Qian et al [2006] has reported a mix comprising 45% fly ash, 5% cement and 50% of industrial sludge could provide the required solidification and stabilization but only achieve a compressive strength of 0.3MPa, confirming the dangers of too little cement content.

7.4.2 Release of Pb after addition of 30% PFA to OPC

The release of Pb from a specimen 50mm cube containing 70% OPC and 30% PFA is presented in Table 7.8 (See Appendences for data of 10 % and 20 % PFA). The release of Pb was measured by ICP, and for 13 of the 21 measurements the level was undetectable. There is a peak at 72h (the amount leached over the previous 48 hours) of 1.56μg/cm^3. However, given the range of the measured values this might be due more to experimental procedure than Pb actually leaching away. What is absolutely clear from Figure 7.14 is that less Pb leaches away when PFA has been added to the OPC compared to the amount that leached away with OPC alone, about 5.4 x 10^{-4}g compared to 15.8 x 10^{-4}g.

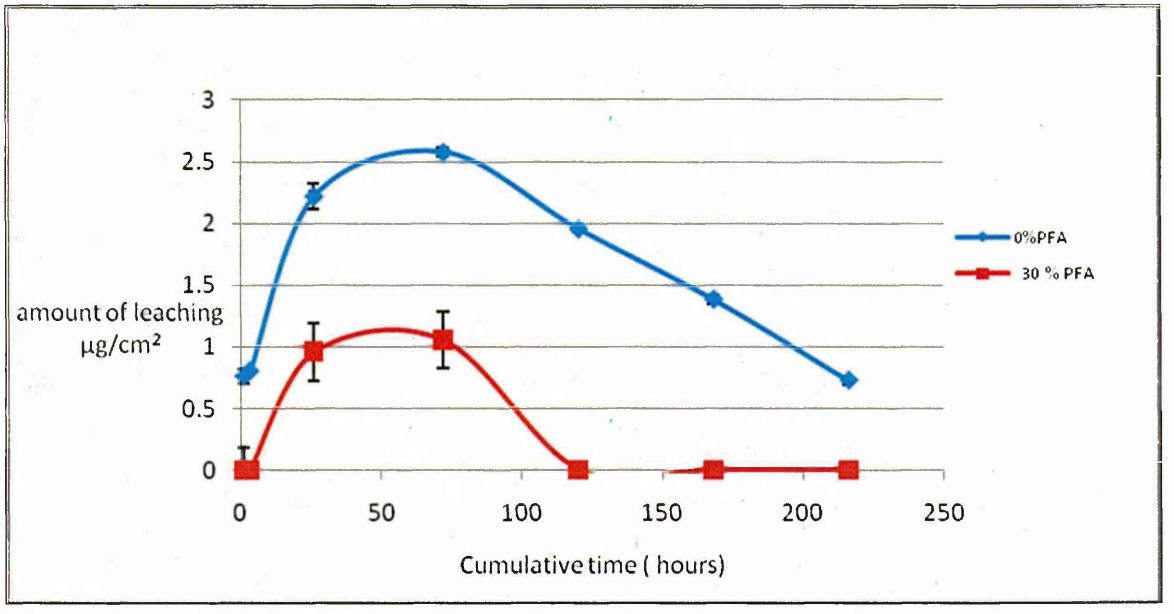

Figure 7. 14 Cumulative release of Pb (μg/cm^2)(n=3) as function of time during tank leaching test (0% PFA+100% OPC and70 % OPC +30% PFA 50mm cube)

Table 7. 8 Cumulative leaching of Pb as a function of time during the tank leaching test (70% OPC and 30% PFA, 50mm cube)

Total duration of immersion of OPC block in leachant (DI water) (hours)	Time between tests (duration of leachant in tank) (hours)	Tank 1 Pb (mg/l)	Tank 2 Pb (mg/l)	Tank3 Pb (mg/l)	Mean Pb (mg/l)	sd	Mean Pb ($\mu g/cm^2$)	Mean Pb ($\mu g/cm^2/h$)
1	*1*	0.056	ND	0.33	0.19	0.39	0.78	0.78
3	*2*	ND	ND	ND	ND	-	ND	ND
24	*24*	0.47	0.015	0.19	0.23	0.23	0.92	0.04
72	*48*	0.32	ND	0.44	0.38	0.24	1.56	0.03
120	*72*	0.06	ND	ND	0.06	0	0.25	5×10^{-3}
168	*96*	ND	ND	ND	ND	-	ND	ND
216	*120*	ND	ND	ND	ND	-	ND	ND
Total lead leached out		5.4×10^{-4}g					3.5 $\mu g/cm^2$	

ND = None Detected

Table 7.9 pH as a function of time in the leachant (renewable tank leaching test, 70% OPC + 30% PFA cube)

Total duration of immersion of OPC block in leachant (DI water) (hours)	Time between tests (duration of leachant in tank) (hours)	pH Tank 1	pH Tank 2	pH Tank 3	Mean pH	sd
1	*1*	11.97	11.86	12.14	12	0.14
3	*2*	11.73	11.66	11.95	11.8	0.15
24	*21*	12.2	12.23	12.42	12.3	0.12
72	*48*	12.28	12.28	12.3	12.3	0.01
120	*48*	12.11	12.18	-	12.1	0.05
168	*48*	12.08	12.04	12.1	12.1	0.03
216	*48*	12.07	12.04	12.13	12.1	0.05

From Figure 7.15 it can be seen that the highest pH level 12.3 release of Pb reached the peak at 48h at 1.56 $\mu g/cm^2$, see Table. 7.8 None PFA samples had pH levels were between 11.8 - 12.3. Figure 7.14 shows that the pH of samples containing a greater amount of PFA has a high, pH 12-12.3, and reached the peak 12.3 at 24h interval. Compared with no PFA (100% OPC) reached during the tank test from pH 11.8-12.1, the highest pH was 12.07, at 24h.

However, in comparison with samples with PFA and No PFA samples at both72h and 216h, At 72h there is not a significant difference in the pH levels, whereas at 216h there is. With 30% PFA and 70% OPC the total release of Ca is clearly very much less than for 100% OPC, 0.82g compared to 57.1g. This difference persisted over the duration of the leaching process; see Figure 7.16 and Table 7. 10. The difference is explained by the greater CaO content of the OPC (about 60% of the OPC) see XRF analysis Chapter 2.

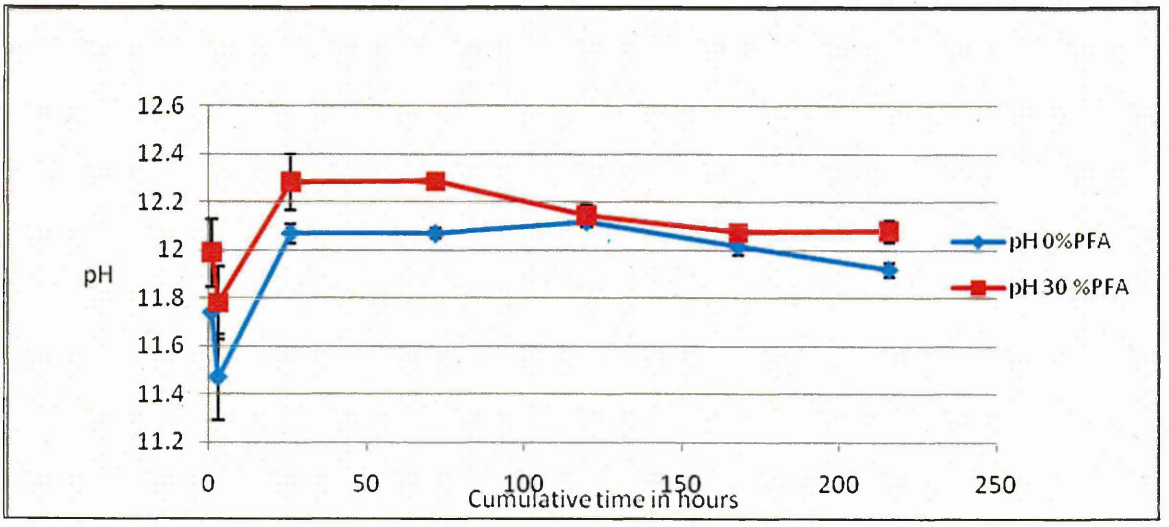

Figure 7. 15 pH Level as a function of time (renewable tank leaching test,0% PFA+100% OPC only and 70% OPC + 30% PFA cubes)

7.4.3 Release of Ca after addition of 30% PFA to OPC

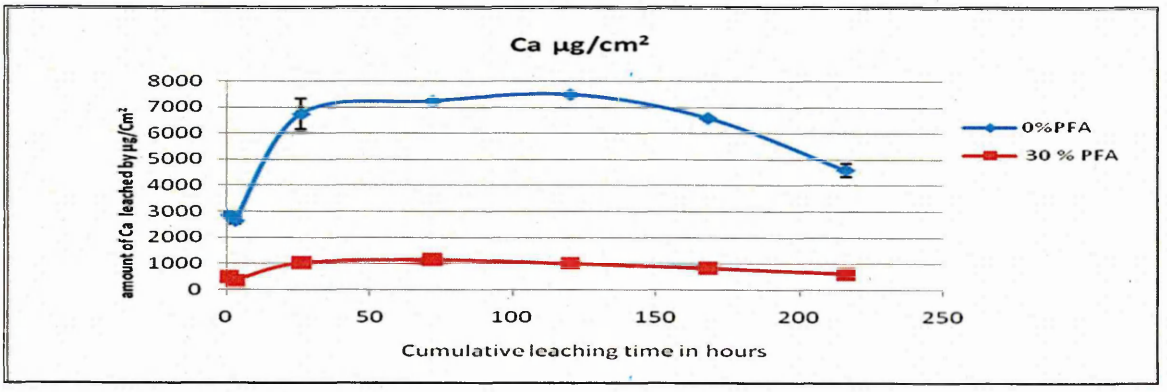

Figure 7.16 Cumulative leaching of Ca (µg/cm^2) (n=3) as function of time during tank leaching test (0% PFA +100% OPC + 30% PFA+70% OPC 50mm cube)

Table 7. 10 Cumulative release of Ca at varied time intervals during the tank leaching test (70% OPC and 30% PFA, 50mm cube)

Total duration of immersion of OPC block in leachant (DI water) (hours)	Time between tests (duration of leachant in tank) (hours)	Tank 1 Ca (mg/l)	Tank 2 Ca (mg/l)	Tank 3 Ca (mg/l)	Mean (mg/l)	sd	Mean Ca ($\mu g/cm^2$)	Mean Ca ($\mu g/cm^2/h$)
1	*1*	120.7	91.7	137.8	117	23.3	486.3	486.3
3	*2*	63.8	75.3	111.1	83.4	24.7	347.4	173.7
24	*21*	212.4	203.6	325.7	247	68.1	1030	46.8
72	*48*	287.6	255.3	290.0	278	19.4	1157	24.1
120	*48*	262.2	195.9	269.0	242	40.4	1010	21.0
168	*48*	191.1	168.6	241.6	200	37.3	835.2	17.4
216	*48*	141.6	124.6	180.3	149	28.6	620.3	12.9
Total Ca leached out		0.82g						

According to Barna et.al [2001]The Ca present in the leachate mainly comes from dissolution of the portlandite generated in the material by the hydraulic binder's hydration. Calcium silicate hydrates are not considered because they are less soluble than portlandite. Two species of soluble calcium are considered: Ca^{2+} (hydrated ion) and the complex $CaOH^{+}$.The precipitated forms of calcium are portlandite $Ca(OH)_2$ and calcium carbonate $CaCO_3$.

7.4.4 Release of Sodium and Potassium after addition of 30% PFA to OPC

It is clear that the addition of PFA increases the release of Na substantially up to at least 120 hours. After that the differences in the release rates tend to narrow and all approach about $2.0\mu g/cm^3/h$.

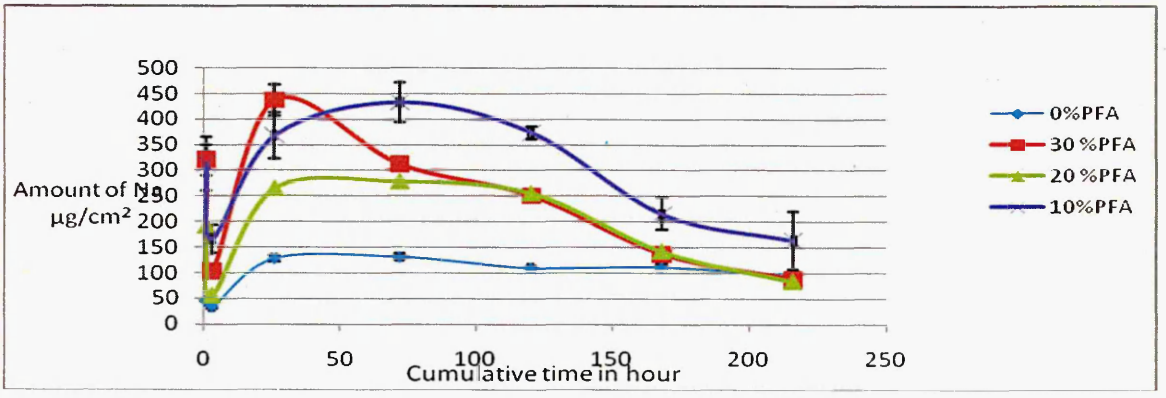

Figure 7. 17 Cumulative leaching of Na ($\mu g/cm^2$) (n=3) as function of time during renewable tank leaching test (0% PFA +100% OPC, 70% OPC+ 30% PFA, 80% OPC + 20% PFA, and 90% OPC + 10% PFA ,50mm cube)

The higher release of Na in samples containing PFA is compatible with higher pH measurement of pH. The amount of Na released caused by increase in pH (see Figure7.17 and 7.18 and Table 23 in appendix), which shows the results for measurement of Na in this study. There was more release of Na samples containing PFA compared with no PFA samples. The amount of Na released increased, but the amount of K release decreased a similar to study reported by Paine et al [2002] also Barna.et al.[2005] observed a similar relationship with pH of elute and the amount of Na and K.

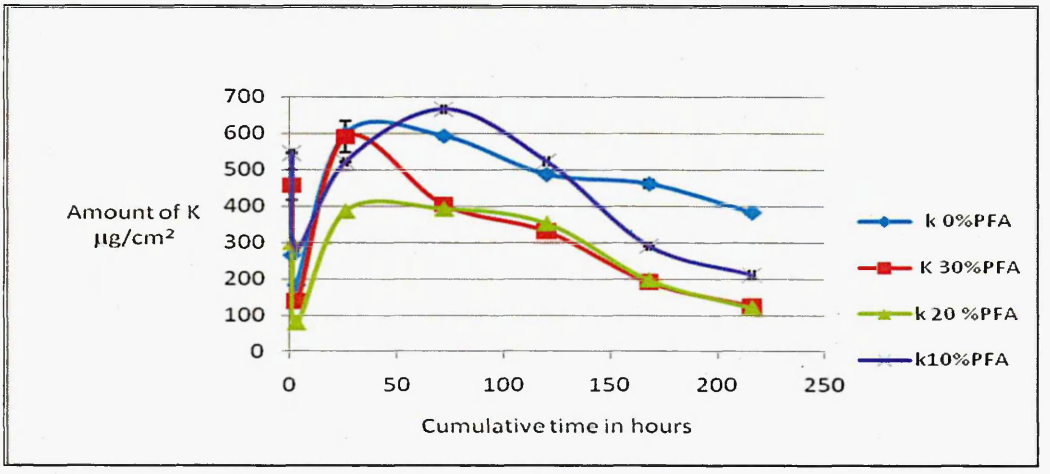

Figure 7.18 Cumulative release of K (µg/cm^2)(n=3)as function of time during tank leaching test (0% PFA +100% OPC,70% OPC + 30% PFA, 80% OPC+20% PFA, and 90% OPC + 10% PFA ,50mm cube)

The total amount of K released during the 216h of the leaching process fell from 0.446g with 100% OPC to 0.36g with the addition of 30%FPA to the mix. Also the rate of release appears to be less for the entire process after the PFA was added. See Fig.7.18 and Table 24 in appendix for K cumulative release in this study. However, K/Na-ratio of the cements indicates that the differences in expansion are due to the differences in the cationic composition of the pore solution. According to Leemann and Lothenbach [2008] reported that cracks of quartzite reflects the different in K/Na ratio.

7.4.5 The effect of addition of PFA on Aluminium release

The release of Al was measured by ICP. Figure 7.19 and (Table 25 in appendix) show that the total release of Al over the 216h leaching period increased from 2.43x10^{-3}g to 3.38x10^{-3}g when 30% PFA is added to the OPC. Initially the rates of release appear much the same, but as the leaching period gets longer the aluminium leaches at a greater rate in the presence of PFA until at the end of the leaching period the rate of release in the presence of PFA was

0.11µg/cm^2/h compared to 0.09µg/cm^2/h for 100% OPC. However Several authors [Melissa et al 2010, Helal. 2006, Jacob..et al 2005] affirmed that the leaching of Al is controlled by amorphous $Al(OH)_3$ for pH ranging between 6 and 9, by gibbsite ($Al(OH)_3$.

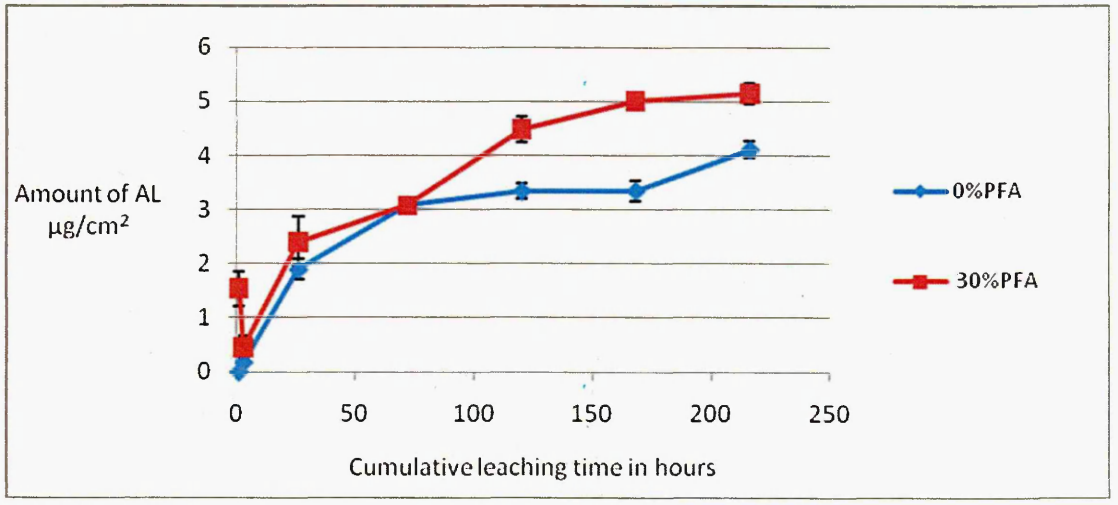

Figure 7. 19 Cumulative release of Al (µg/cm^2) (n=3) as function of time during tank leaching test (0% PFA+100% OPC and 30 % PFA+70% OPC 50mm cube)

7.4.6 The effect of addition of PFA on Cl^-, NO_3^-, and sulphate SO_4^{2-} release.

Figure 7.20 and Table 26 in appendix show the results for the leaching of sulphates when 30% PFA was added to the OPC. The release of sulphate in the first hour appears to be much higher in the presence of PFA. However, the difference is not significant (at least at a 95% confidence level) because the range of measurements (65.8mg/l, 21.6mg/l and 43.7mg/l) is so wide and the standard deviation so large (22.1mg/l) that the difference in the mean values at the end of the first hour cannot be taken as an indication that the release of SO_4^{-2} is initially higher when PFA is present.

A comparison of mean values shows only one significant difference at better than the 95% level of confidence. That difference occurs in the readings taken at 120 h and shows that the reading with 30% PFA is lower than the reading with 100% OPC. However, overall there was a greater amount of sulphate leached out when PFA was added than for 100% OPC, 0.033g compared to 0.012g.Miletić et al [1997] have reported that addition of PFA can be useful for preventing sulphate corrosion of concrete even in the case of very strong ammonium-sulphate corrosion.

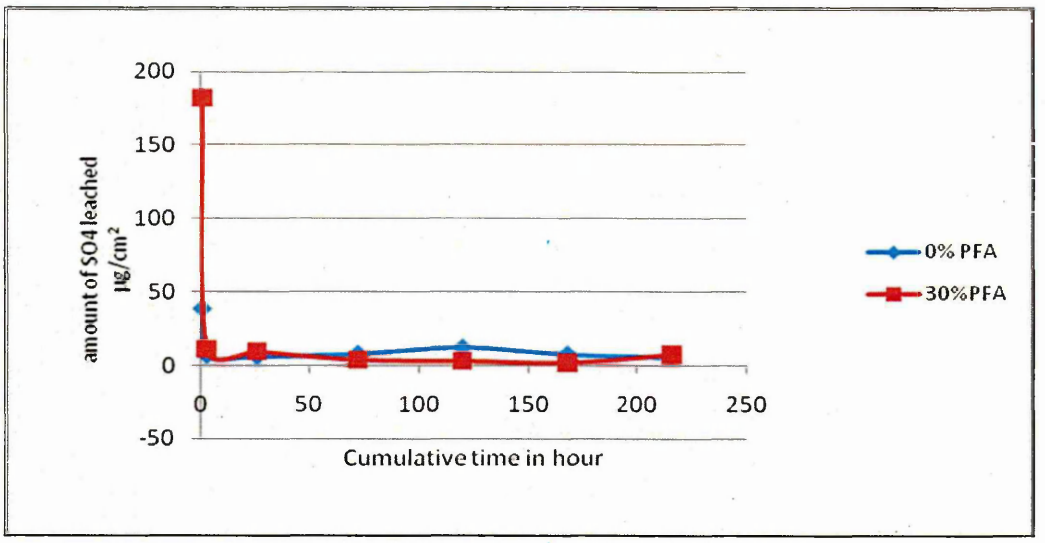

Figure 7.19 20 cumulative leaching of Sulphate ($\mu g/cm^2$)(n=3) as function of time during tank leaching test (70% OPC + 30% PFA 50mm cube)

At first contact between the material (OPC and PFA) and water the release was high then fell sharply and reached equilibrium state of SO_4^{2-} a similar trend as reported by Barna. et al[2001]. A soluble fraction coming from a small quantity of gypsum ($CaSO_4 \cdot 2H_2O$) can explain the pH-independent concentration of SO_4^{2-}, at the first hour the pH were 12, (see Fig 7. 15, Table 26). Karamalidis and Voudrias..[2008] support this trend of the results.

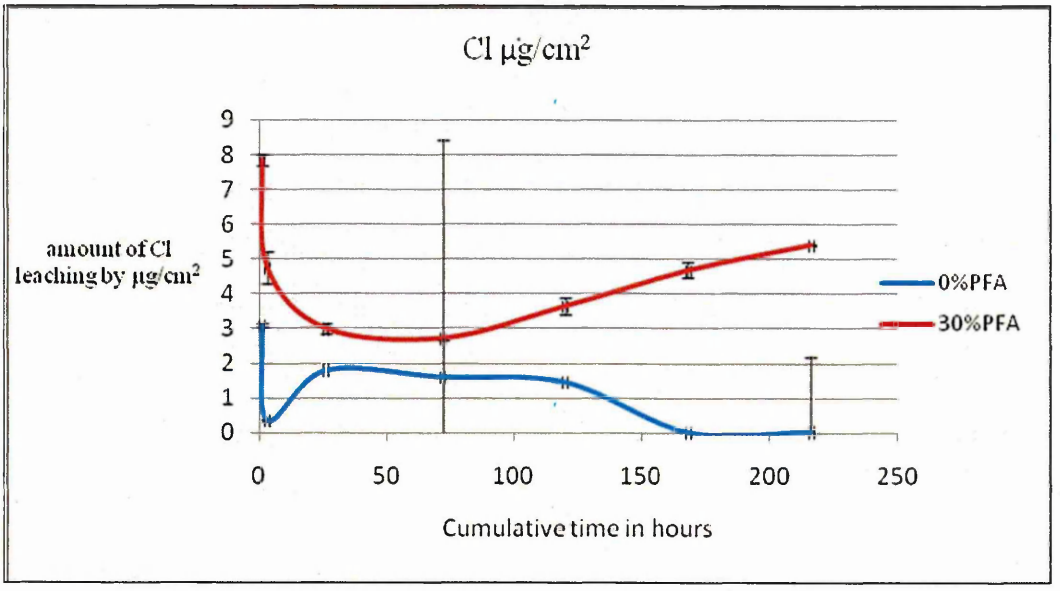

Figure 7.20 21 Cumulative release of Cl^- ($\mu g/cm^2$)(n=3) as function of time during tank leaching test (70% OPC + 30% PFA 50mm cube)

In Figure 7. 21 and Table 27 in appendix, it can be seen that the release of Cl is substantially higher overall when 30% PFA is added to the OPC, the amount released increases more than threefold from $1.3x10^{-3}$g to $4.8x10^{-3}$g. The trend is interesting as the rate of release of Cl^- when 30% PFA is present increases with time. Many researchers have concluded that the amount of bound chloride decreased with increasing concentration from the cements and that the amount of free chloride decreased with increasing C3A. Barna.et al [2001] reported that fly ash from MSW incineration solidified in the material have a high chloride content, which induces a pH value less than 12 in the pore water. During the leaching test also the concentration of Cl solubilised was of the same order of magnitude as the Na and K concentration, Gao et al [2008] reported that some types of PFA contain more Cl^- than others have none PFA, Chlorine is one of the steel corrosion substances which will affect the strength of the specimen .

In Figure 7.22 and Table 28 in appendixes, the measured release of NO_3^- appears almost constant when there is 30% PFA added to the OPC. The curve with no added PFA begins from an initial low level, rises to a peak at 120h and then falls. The initial two readings with PFA are significantly lower than those without PFA, while at 120h the reading without PFA is significantly higher than the reading made with PFA. The other four readings do not show any significant differences.

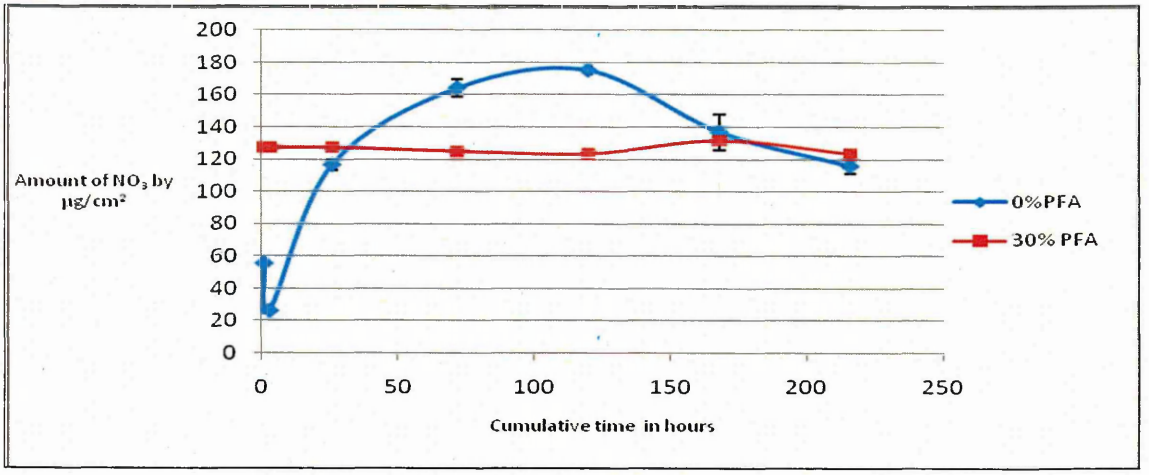

Figure 7.22 Cumulative leaching of nitrate µg/cm^2)(n=3) as a function of time during tank leaching test (70% OPC + 30% PFA 50mm cube)

7.4.7 Effect of curing on compressive strength of the cube, with and without added PFA

Malviy and Chaudhary [2006] have reported that the compressive strength of a cement mix is determined more by its constituents than the water/cement ratio (W/C). This confirms the conclusions of others [Rossetti, et al 2002; Chisholm and Lee 2000] that the cement content and curing process are the most important factors in determining compressive strength, with the water-to-solids ratio being significantly less important. Extended curing and high humidity generally increases strength.

The W/C is a factor affecting the compressive strength of the cured concrete, a water/binder ratio of 0.4–0.5 and a water/solid ratio of 0.4–0.6 are generally used, with the exact value depending upon the type of waste being solidified though super plasticisers may be added to improve fluidity and to reduce water/binder ratio [Malviy and Chaudhary 2006]. Water to binder ratio is the main factor that control strength development of concrete. Concrete with lower water/binder ratio is mostly denser and has higher strength. [Prasad.et al 2006]. In this study the W/C ratio used was 0.4, see Section 2.2.3. Andac and Glasser [1999] used the same ratio and adopted the same procedure on the grounds that it had been used in many previous studies.

However, when PFA is mixed with the OPC, the water requirement of the mix increases and a decrease in compressive strength was observed. Similar results have been reported for steel finishing unit sludge and OPC, where the lower strength resulted from the lower OPC content and much higher water content [Pandey and Sharma, 2000].

Figure 7.23 the measured compressive strengths, in MPa, for the different cubes. There were four lengths of the curing time: 7days, 14 days, 21 days and 28 days. There were four different mixes used, 100% OPC, 10% PFA+90% OPC, 20% PFA+80% OPC and 30% PFA+70% OPC. The results show that the unconfined compressive strengths of all four materials for all four curing times met the US EPA regulatory limit of 0.35MPa for S/S materials. In the UK the acceptable 28-day strength is 0.7MPa but a figure as low as 0.35MPa may be considered depending on the test specimen [Malviya and Chaudhary, 2006]. Figure 7. 23 an increase in strength with increase of time of curing was seen for all four specimens. This is a commonly observed phenomenon and confirms the fact that curing time is an important factor affecting unconfined compressive strength [Srivastava et al 2008; Malviy and Chaudhary,2006].

In this study it was found that after 7 days curing, the highest strength was for the 100% OPC sample - 23MPa, and the lowest strength was for the 30% PFA+70% OPC sample - 19MPa. The samples cured for 28 days had a maximum unconfined compressive strength of 37MPa (100% OPC) and a minimum unconfined compressive strength of 34MPa (30%PFA+70%OPC). Qian et al [2008] have reported 28 MPa after 28 days curing for OPC-Pb, which is slightly lower than the figure obtained in this study.

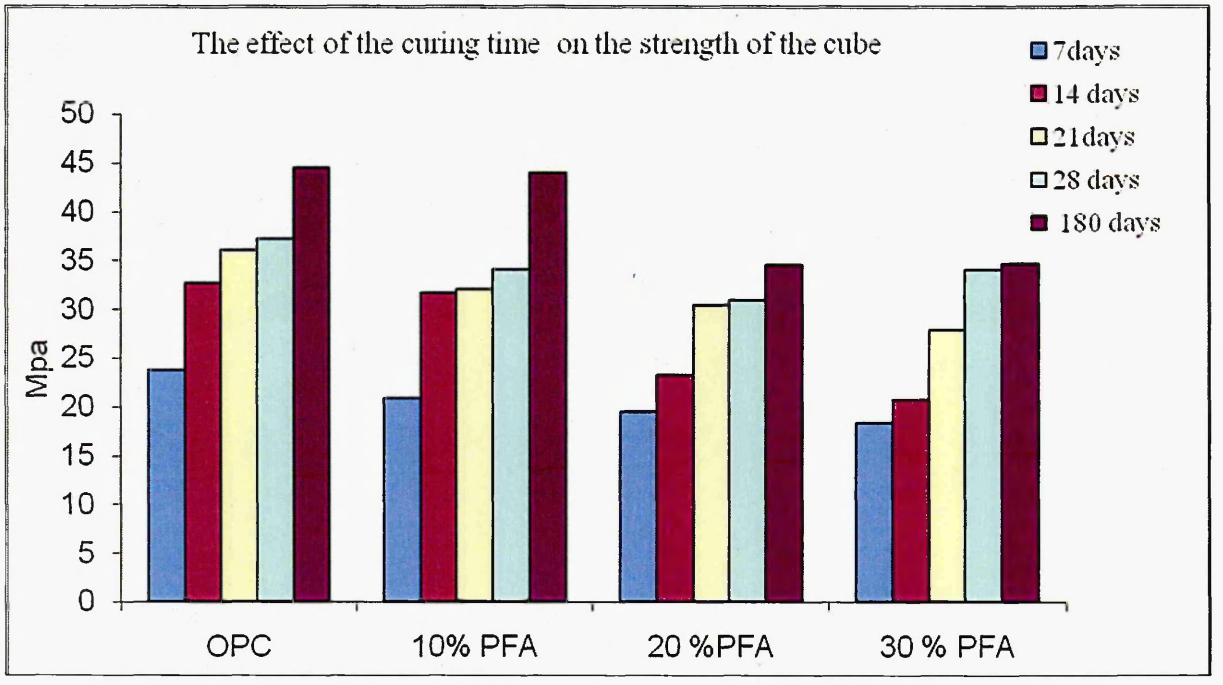

Figure 7.23 Unconfined compressive strength of the PFA+OPC samples for different proportions of PFA and four different curing times

Lee et al, [2003] used (thermo gravimetric analysis) TG analysis to determine the amount of CaOH. TGA was used in this study to determine the amounts of $Ca(OH)_2$ present in the samples at 1,7, and 28 days, and found that with no PFA present the amount of $Ca(OH)_2$ in cement pastes continuously increased for the whole 28 days. Cement pastes containing 40% of PFA had nearly 50% less $Ca(OH)_2$ than cement pastes without PFA. The effect of PFA content on the strength is quite clear, in Fig. 7.23 it shows that increasing the content of PFA in the cube decreases the strength of the cube, similar results were reported by [Cheng et al 2000].

Qian et al., [2008] reported that OPC–Pb had the highest unconfined compressive strength (compared to OPC with PFA) of 41.3MPa at 3 days and 81.4MPa at 28 days. (Pb-doped CSA cement matrix) OPC-Pb displayed a good early strength of 40MPa at 1 day, the same as that

of OPC–Pb at 3 days. As stated above, in this study 100% OPC gave 23 MPa at 7 days and 37 MPa at 28 days and still had the greatest compressive strength of 45MPa after 180 days (see Figure 7.24) OPC mixed with 30 %PFA at 28 days 34Mpa in this study which was similar to rate reported by Qian et al., [2008].

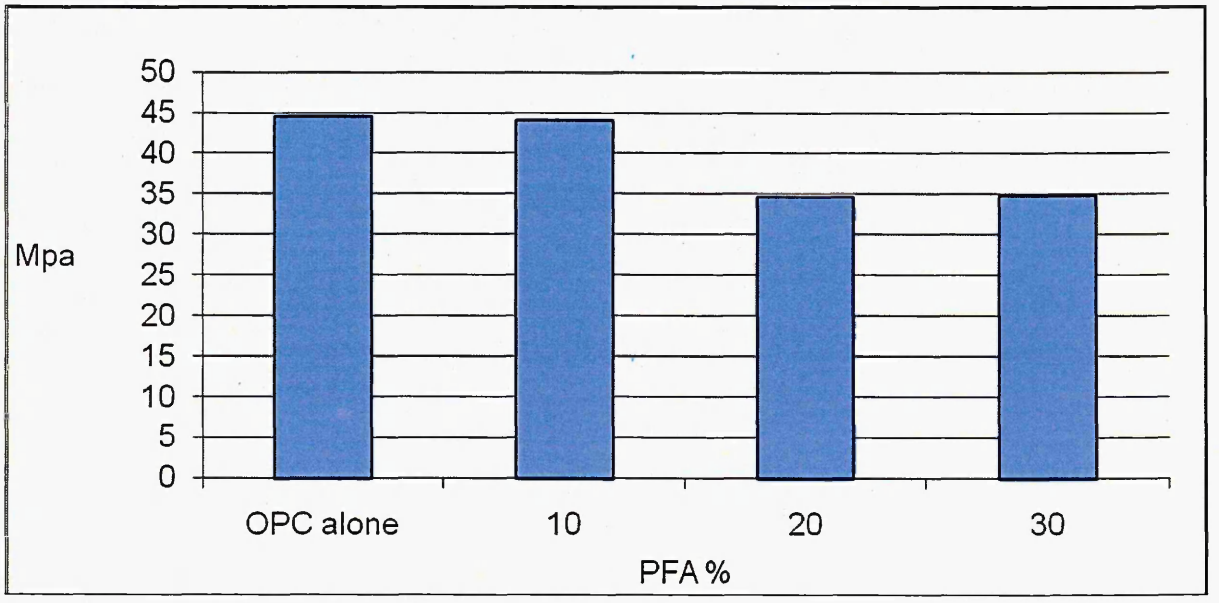

Figure 7. 24 Effect of percentage PFA on compressive strength of OPC cube after curing for 180 days

7.4.8 The effect of water absorption and water loss on OPC and OPC + PFA cubes

Figure 7.24 shows the effect of prolonged heating on the mass of the test cubes. After de-moulding the cube it was cured for 7 days, the cube weight measured in grams and then placed in an electrical oven and left it for optimum times at each interval, the weight measurement were taken at 1 hour, 2 hours and then after 3, 5, 7, 9, 11 and 13 hours. The internal temperature of the oven remained between 80 and 84°C. The loss of mass of the cubes was assumed to be due to water loss after investigating the effect of drying on the cubic sample. For measuring the rate of water absorption of the cube the procedure was that prior to immersing the sample in water to investigate the effect of cooling on samples the weight was measured at 0 h, 1 h to 26 h (see Figure 7. 26). Singh et al,[1990] are in agreement with this trend of the results, however, Bentz [2002] reported that cement pastes, with fly ash additions are more sensitive to curing conditions than those without, most likely due to a decrease in initial hydration reaction rates.

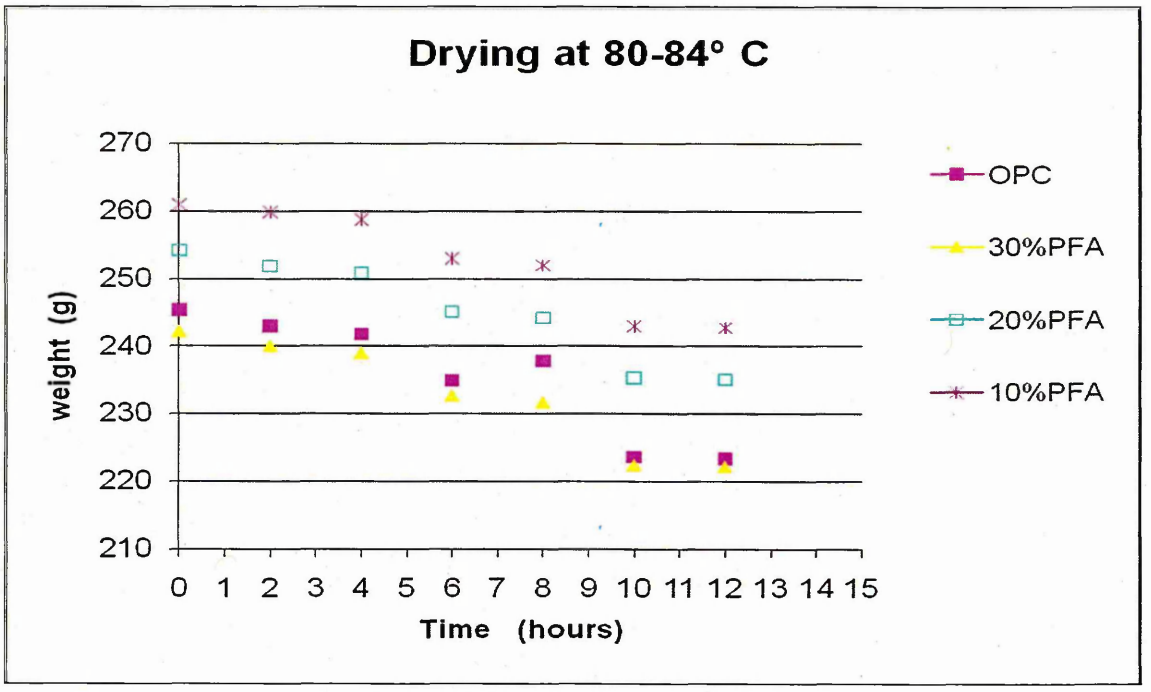

Figure 7.25 Effect of drying on the mass of OPC cube with varied amount of PFA (n=3)

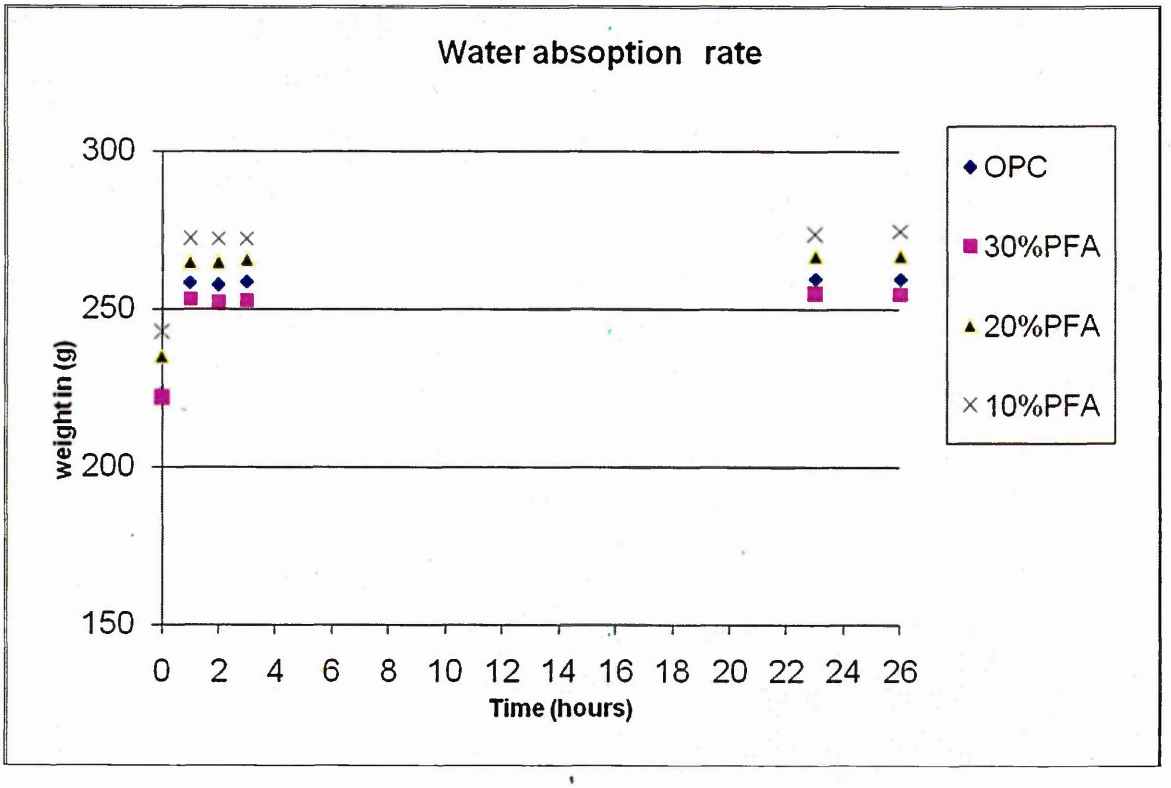

Figure 7.26 Effect of water absorption on mass of OPC cube with varied amount of PFA (n=3)

7.4.9 The acid extraction test for Pb from OPC cube.

Extraction tests are usually designed to reach a steady-state release, termed "equilibrium". Equilibrium-based leaching protocols typically require particle size reduction of the material under study, in order to reduce the time required to obtain steady-state release via increased surface area and minimized kinetic transport [Spence and Shi2005]. In agitated extraction, shaking or stirring further accelerates the extraction rate and ensures continuous solid/liquid contact. Common equilibrium tests are: single batch extraction, parallel batch extraction, sequential-batch extraction and concentration build-up extraction [Spence and Shi 2005].

Digestion tests were performed to determine how much available contaminant is in the samples Here samples (OPC stabilized Pb) of mass 0.5g, that dissolved in acid with heating for 10 or 30min were used The availability of the contaminant was identified by acid digestion test for 1 g of OPC and using XRF before and after immersing the specimen in the tank.

The amount of 0.5g of OPC which extracted 1318μg/g was multiplied by 2 to give 1g OPC. e.i 2636 μg/g of Pb was extracted and the average of weight of the sample was 200 g wet powder of OPC, (see Section 2.2.5). In Table 7.11 the maximum extractions were achieved for OPC were 805 μg/g followed by 820 μg/g for 30 % PFA replaced OPC, then 20 % PFA replaced OPC, 807 μg/g and 811 μg/g for 10 % PFA.

Table 7.11 Acid digestion test results for varied samples (OPC+/-PFA) for 30 min with HNO_3

sample	Tank 1 mg/l	Tank 2 mg/l	Tank 3 mg/l	Vol ml	solid g	mass of Pb μg/g	mass of Pb μg/g	mass of Pb μg/g	Mean
OPC	15.12	15.39	17.79	25	0.5	756.0	769.5	889.5	805.0
30%PFA+70%OPC	22.68	12.92	13.6	25	0.5	1134	646.0	680.0	820.0
20%PFA+80%OPC	18.81	13.69	15.94	25	0.5	940.5	684.4	797.0	807.3
10%PFA+90%OPC	10.94	21.53	-	25	0.5	547.0	1076.5	-	811.8

Chapter Eight

Conclusion and Future work

8.1 General discussion and Conclusion

From the results presented in this thesis it is clear that additions of PFA, lime and magnesia assist the retention of metals, including Pb, Zn, Cd, Cu, Cr, Ni, Al and Fe in treated soils. Data presented in the summary tables in this chapter confirm that over 50 % retention occurred provided the pH of the solutions was greater than 6.4, while in chapter 7 it was shown that for 95% retention of the metals in soils at least 2 % W/V of PFA was required. The use of the same amount of the other stabilisers (OPC, Lime, GGBFS, PFA and magnesia) also gave 95% retention of Pb. It was found in chapter 3 that ordinary Portland cement, if cured for 7 days, was also effective at retaining 99% metals. The effects of reducing the amount of cement used by replacement with PFA and GGBFS were tested as replacement materials. When using OPC alone the maximum retention of lead over the surface of the cube was 10.5μg/cm^2, whereas a 30% replacement with PFA reduced this to 3.5μg/cm^2. The maximum replacement with GGBFS was 50 % which reduced the retention of lead to 0.57μg/cm^2. Thus replacement with GGBFS and PFA was more effective in reducing the amount of Pb leached out compared with OPC alone. The unconfined compressive strength measurements described in Section 7.4.7 showed that OPC alone had a strength of 23 MPa after 7 days curing which means that the material would be usable for environmental standard procedure as detailed in section 7.4.7. This was reduced to 19MPa for 30 % PFA replacement of OPC. The values for samples cured for 28 days were 37MPa and 34MPa respectively.

Chapters 3 to 7 described the characterization of the products of the reaction between the metals and the stabilizers. A variety of low solubility compounds were present which were shown by ESEM, EDX and XPS to contain Pb. XRD was found to be a useful tool to identify the compounds, including $PbSiO_3$, Pb_2SO_4, $PbCO_3$ formed by the interaction of OPC and Pb in solution. The addition of PFA caused Pb_2O (CO_3) to be formed, whereas with lime the compounds formed were PbO, Pb_2CO_3, $PbCO_3$, Pb_2CO_3, $Pb_2O(CO_3)$, $Ca(PbO_3)$, $PbSO_4$, $Pb(SiO_3)$ and with magnesia they were PbO_2,$PbMg(V_20_7)$,Mg_2Pb, and $PbMg,Mg_5O_4(OH)$. In the case of magnesia, the relatively low peaks on the XRD trace was attributed to the lack of chemical and physical binding between the magnesia and the soil grains, and so chemical species that would have resulted from such binding were absent. The compounds which are formed by PFA interaction with Pb contaminated soils and solution included PbO, PbOH Pb-S_x, $Pb2ALSi_2O_9$, and Pb_2 $FeSi_2O_9$. The addition of GGBFS

produced a distinctive XRD pattern with high background (see Fig.6.5), which included $Pb_4(SO_4)CO_3)_2(OH)_2$ that may have been in the form of a glass.

8.2 Effect of type and amount of stabilized material on leaching of lead contaminated soils

The increase in the amount of lead retained by treated soils was accompanied by an increase of pH of the mix, which as shown in Table 8.1 was independent on the type of the additional material used (OPC , Lime, Magnesia, GGBFS or PFA). The removal of lead from the soils is correlated with increase of pH in the final solution.

The increase of pH and leaching of metal the soil were accompanied by leaching of various amounts of Ca,Na,K, Mg, Cl^-, SO_4, NO_3^- from the system, dependent on the type of stabilizer that had been added . Those elements leached out independent on the stabilizer composition, for instance the Lime contains a high amount of Ca which caused largest release of Ca, followed by cement (see XRF analysis in Table 3.4). The pH in the final solution (leachate) as result of adding lime is 12.4 and for adding cement is 12.2. The Ca release is 4000μg/g and 2000μg/g respectively (see Table. 8.1). However, the amount of leaching was dependent on the pH of the leachant (leaching fluid or solution). The effects of various pH of leaching fluid were investigated by experiments using deionised water, 0.1M HNO_3(pH1.2) and 0.01 M HNO_3 (pH2.2).The relation between the Ca release and pH is not simple. The soil solution pH is dependent on mineral weathering and mineral weathering increases pH by releasing Ca, Mg and K. A soil which is rich in easily weatherable minerals tends to have both a higher pH and higher soil solution concentration of Ca, Mg and K. On the other hand deposition of sulphate, nitrate decrease the pH of soil solution.

Soil chemistry, particularly the Ca content, clearly influences the pH of poorly buffered weak leaching solutions. Changes in soil Ca would be expected to produce corresponding changes in leached element concentrations that may be unrelated to mineralization [Smee et al 1999]

The lowest final pH was 6.2, which still achieved full removal of lead from the leachant from contaminated soil. This was achieved by using 0.1 g of PFA to treat the contaminated soil (see Table 8.1), and was accompanied by increase of the pH were from 5.4 to 6.2. There was no increase in Ca, or Mg. The only remarkable increase was in Na with slight increase in K. This is can be explained by the increase not only of dissolution of Ca, K or Na, but also due to the adsorption capacity of PFA which caused uptake the lead from the soil.

Using magnesia as stabilizer, the amount of Mg in the leachate was greater than with lime, cement, PFA, or GGBF, see table 8.1. In this case the pH of the leachate was 10.4 and the release of Mg was250 μg/g. The Ca released was only 190 μg/g, the increase in Ca was only 10 μg/g compared with non treated soils. It is noteworthy that use of OPC or lime, which released primarily Ca^{2+}, resulted in a larger increase in pH than when using magnesia, which released primarily Mg^{2+}. However, when measuring the chlorine release when each binder was used, the largest Cl release was observed with OPC, which released 18.0 μg/g. This was approximately twice the 9.5 μg/g released from untreated soil. The next largest release of Cl^- was for contaminated soil stabilised with magnesia, where 11.2 μg/g Cl was released. No change in Cl^- release was observed after adding lime or GGBFS, and only a slight reduction occurred when using PFA to treat the contaminated soils (see Table 8.1). When the release of nitrate was lowest for OPC treated contaminated soil, followed by lime and PFA.

When adding 2% of OPC to treat 5 g of lead contaminated soils, there was a reduction of 99 % in the lead in the elute solution with increase of the pH in the final solution to 12. The greatest amount of retention was obtained when using OPC, where at various pH of leachant the amount of lead in the leachate increased with decrease the pH of the leaching solution. Using 0.01 M HNO_3 as leaching fluid (pH2.2) the amount of lead released was 2.56 μg/g, with 0.1M HNO_3 as leaching fluid (pH1.2) it was 597μg/g, and with deionised water as leaching fluid (pH5.4) there was no detectable lead leached from the contaminated soils amended with OPC , lime, magnesia, GGBFS or PFA.

In comparison, Jing et al [2004] used 25 % cement with TLCP ID water extraction to reduce the Pb released from 5.7 mg/l to 0.7mg/l. Sang et al [2009] used 2-5% of steel furnace slag to amended soil contaminated with metals. They reported 98 % removal of lead, zinc and Cd accompanied by a pH increase from 5.7 to 6.2.

The effect of the initial pH of the leaching solution on the pH of the leachate produced was also monitored. The highest amount of lead leached out from the contaminated soils was with an initial pH of 1.2. No change in the pH of the leachate was observed from contaminated soil amended with stabilizer. The maximum extraction of Pb of 858 μg/g was achieved by using a leaching fluid with a pH equal to 1.2; the maximum extraction was (See Table 8.2). The GGBFS were the most effective as stabilizer. This gave the greatest retention of Pb (100%), followed by magnesia and OPC, 38% and 30% respectively, and 17% reduction with using lime and 8% reduction with using PFA, see Table 8.2.

Table 8.1 Effect of different stabilized materials leached with 50 ml of deionised water as leaching fluid on Pb and associated element release. The data are summarised from chapter3-7.

sample	leaching fluid (pH5.6)	Pb (µg/g)	pH in leachate	Ca (µg/g)	Mg (µg/g)	Na (µg/g)	K (µg/g)	Cl^- (µg/g)	NO_3^- (µg/g)	SO_4^{2-} (µg/g)
Contaminated soil	DI water	37.6	5.4	180	19	5.4	17	9.4	731	25.9
OPC+ Contaminated soil	DI water	0	12.2(11.8)	2000	0	13	82	18.0	569	617
Lime+ contaminated soil	DI water	0	12.4(11.9)	4000	0	0	22	9.5	619	356
Magnesia + contaminated soil	DI water	0	10.4	190	250	2.34	17	11.2	696	221
GGBFS + contaminated Soil	DI water	0	7.5	180	15.4	1.1	19	9.78	666	27.6
PFA+ contaminated soil	DI water	0	6.2	180	17	14.1	20	7.5	612	217

During the batch tests with leaching fluid (pH 2.2) 0.01 M HNO_3, the release from untreated soils was 744 µg/g. Most of the binders reduced the leaching of lead from the final solution by 95-98%; The PFA achieved only a 16 % reduction with no increase of final pH. The lowest pH was 6.2 where the reduction was 98% with using 0.1 g GGBFs as binder. The greatest reductions in lead leaching from contaminated soil were achieved by using magnesia, OPC, Lime and GGBFS respectively (see Table 8.3).

These results are in agreement with Alpalan and Yukselen [2002] who used the TLCP Leaching test to show that lime and cement result in Pb immobilization of 88% efficiency at 1:21 lime: soil ratio and 99% efficiency at 1:15cement: soil ratio, respectively.

In a semi-dynamic tank test, Moon and Dermatas [2007] used 25 % fly ash and achieved 99.8 % reduction in Pb leaching. Berryman et al [2005] used 35% Class C or 25% Class F fly ash to replace the OPC and achieved high performance in strength with 27.5Mpa. Panesa and Chidiac [2009] used 50% GGBFS and reported high physical strength. Duchesne and Laforest, [2006] used 50 % GGBFS which produced a 95.5% reduction in metal leaching.

Table 8.2 Effect of different stabilized material leached with 50 ml of 0.1MHNO$_3$ (pH2.1) as leaching fluid on Pb and associated element release. Data summarised from chapter3-7.

sample	leaching fluid (pH.1.2)	Pb (µg/g)	Reduction %	pH in leachat	Ca (µg/g)	Mg (µg/g)	Na (µg/g)	K (µg/g)
soil	0.1MHNO$_3$	858		1.2	2600	280	5	22.1
OPC+ soil	0.1MHNO$_3$	597	30.4 %	1,2	44882	403	37	102
Lime+ soil	0.1MHNO$_3$	711	17.1%	1,2	51000	320	9.3	22
Magnesia +soil	0.1MHNO$_3$	531	38.1%	1.2	2000	24000	9.3	20
GGBFS +Soil	0.1MHNO$_3$	N/D	100%	1.2	30002.3	2500	40.1	92
PFA+ soil	0.1MHNO$_3$	786	8.3%	1.2	3500	330	23.8	41

Table 8.3 Effect of different stabilized material leached with 50 ml of 0.01MHNO$_3$ (pH 2.2) as leaching fluid on Pb and associated element release. Data summarised from chapter3-7.

sample	leaching fluid (pH2.2)	Pb (µg/g)	Reduction %	pH in final solution	Ca (µg/g)	Mg (µg/g)	Na (µg/g)	K (µg/g)
contaminated soil	0.01MHNO$_3$	744		2.2	2400	270	4	19.6
OPC+ contaminated soil	0.01MHNO$_3$	2.6	99.6 %	11.9	19900	0	25	85
Lime+ contaminated soil	0.01MHNO$_3$	3.2	99.5 %	11.92	22000	0	4	20
Magnesia + contaminated soil	0.01MHNO$_3$	1.14	99.8 5 %	9.45	1350	3050	5.4	30
GGBFS + contaminated Soil	0.01MHNO$_3$	7.03	99.05 %	6.3	8500	710	12	35
PFA+ contaminated soil	0.01MHNO$_3$	622	16.4 %	2.2	2800	370	29	29

To the knowledge of this investigator, one of the main contributions of the work presented in this study is the use of a range of investigation techniques on a single soil system. A comparable study has apparently not been reported previously in the literature. Here, Raman, FTIR, XRD, XPS and ESEM have been used to investigate the chemical interaction between the contaminant and the stabilizer and in addition, the factors which affect the performance of the batch test have been investigated, apparently for the first time. The shape of the specimen used was cubic rather than a conventional cylinder shape. In addition the amount of the stabilizer material added to the contaminated system was optimised. The amount of stabilized material that was found to be optimum was 2% in this study and no similar reports are known in the literature for a batch test system. Also, the amount of replaced cement investigated in the tank leaching test system was unique in terms of the procedure. The types of compounds formed by interaction between the stabilizer and contaminant have been identified using XRD combined with other techniques, especially for the magnesia system.

To conclude from the results obtained throughout this study, it is recommended S/S technology should be tested in large scale remediation trails, since it reduces the metal availability in soils and solutions to almost an undetectable level. The successful use of S/S depends on considering the optimum amount of stabilized material, liquid to solid ratio and maintaining the pH to a value of 6.2 or more. Although OPC, lime and Mg are not cheap materials, they can be blended with waste materials such as PFA or GGBS which has been shown to have higher efficiency in reducing the concentration of the contaminant to acceptable levels whilst the physical performance of the final products is also acceptable. Using of S/S will allow advantage to be taken of the reuse of the contaminated sites for reconstruction or redevelopment.

8.2 Future work

Future work should include detailed analysis of the factors affecting the remediation process, such as pH, adsorption capacity and curing time. Also, more analysis is required of factors affecting the amount of leaching such as contact time and S/L ratio, e.g. ratio of S/L greater than 1:60. In the batch test should be used to examine OPC contaminated with Pb and OPC plus waste materials such as fly ash (PFA) or ground blast furnace slag (GBBFS) contaminated with Pb or other metals.

Also further experiments should be conducted on unconfined compressive strength tests on samples containing GGBFS and characterizing the samples which contain GGBFS and OPC

cube. Characterization using XPS, ESEM, EDX, FTIR, and Raman should be included and the same sample should be assessed by TGA instrumentation to measure the heat capacity, temperature and thermal conductivity. The same procedures should be used to characterise the contaminated soil samples used in tank leaching tests and the optimum water content and dry density in each type of soil should be determined. Similarly the same samples should be run on the column leaching test. Finally the wide range of investigations and analytical techniques described in this thesis could be applied to different metals and organic contaminants. Also the effect of using greater amount of a wider range of waste materials on the leaching of pollutants could be investigated.

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Appendix 1

Table 1 Effect of S/L ratio on amount of Pb leached out from contaminated soils

Sample and S/L ratio	Conc. (mg/l)	Mean (mg/l)	Sd (mg/l)	Conc. (µg/g)	Mean (µg/g)	Sd (µg/g)	Comments
1:5							5g soil
contaminated Soil	3			15			
contaminated Soil	1.7	2.3	0.54	8.8	11.3	1.5	25ml
contaminated Soil	1.9			9.7			
contaminated Soil	2.3			11.8			
1:10							
contaminated Soil	3.4			34.0			
contaminated Soil	3.3			33.5	37.64		
contaminated Soil	3.9	3.7	0.81	39.0	36.6	1.2	50ml
contaminated Soil	3.1			31.7			
contaminated Soil	4.5			45.0			
1:20							
contaminated soil	1.3			25.2			
contaminated soil	2.3			45.4			
contaminated soil	2.2	1.6	0.55	43.2	32.2	0.8	100ml
contaminated soil	1.2			23.6			
contaminated soil	1.2			23.8			
1:40							
contaminated soil	1.1			43.2			
contaminated soil	1.0			39.9			
contaminated soil	0.8	0.9	0.41	30.8	34.8	6.3	200ml
contaminated soil	0.2			8.3			
contaminated soil	1.3			51.6			

Table 2 Effect of contact time on leaching of lead contaminated soils with leaching solution of 50 ml Di water

Duration	Conc. of lead (mg/l)	Mean (mg/l)	Sd mg/l	Conc. (µg/g)	Mean (µg/g)	Sd	Comments
0 - 2h							150 rpm
1	2.7			27.1			
2	3.6	3.4	0.57	35.9	33.6	5.7	
3	3.8			37.9			
4							
6 - 8h							
1	4.5			45.2			
2	3.6	3.7	0.76	36.3	37.2	7.6	
3	3.0			30.1			
4							
16 - 18h							
1	1.0			9.5			
2	1.0	0.69	0.5	10.1	6.9	0.40	
3	0.1			1.1			
4							
5							
22 - 24h							
1	0.9			8.8			
2	0.1	0.52	0.31	1.2	5.2	3.1	
3	0.6			5.8			
4	0.5			5.2			
46 - 48h							
1	0.1			0.9			
2	0.8	0.55	0.41	7.6	5.5	4.1	
3	0.8			8.2			
4							
70 - 72h							
1	0.03			0.3			
2	0.30	0.34	0.33	3.0	3.4	3.3	
3	0.70			6.9			
4	N/D						

Table 3 Effect on concentration of lead in solution by addition of NaOH and OPC

Sample	pH of leachant adjusted by addition of NaOH	pH after being shaken for 2 hours	Lead concentration after being shaken for 2 hours, mg/l
10mg/l of Pb	**2.5** *	2.5	9.3
10mg/l of Pb	**2.54** *	2.5	9.7
10mg/l of Pb	**2.54** *	2.6	9.8
10mg/l of Pb + 0.1g of PFA + NaOH	9.3	7.1	0.2
10mg/l of Pb + 0.1g of PFA + NaOH	5.1	6.3	0.2
10mg/l of Pb + 0.1g of PFA + NaOH	6.6	5.5	0.9
10mg/l of Pb + 0.1g of PF + NaOH	7.9	6.8	0.9
10mg/l of Pb + 0.1g of PFA + NaOH	5.6	6.2	0.2
10mg/l of Pb + 0.1g of PFA + **NaOH**	8.9	6.9	0.6
OPC + DI water		12.6	
OPC + DI water		12.7	
OPC + DI water		12.4	

PFA.: Pulverized fly ash,* **No added NaOH**

Table 4 cumulative leaching of Na (n=3) at varied time (renewable tank leaching test) for 100% OPC +0%PFA or 0%GGBFS) 50mm cubes

Total duration of immersion of OPC block in leachant (DI water) (hours)	Time between tests (duration of leachant in tank) (hours)	Tank 1 Na (mg/l)	Tank 2 Na (mg/l)	Tank 3 Na (mg/l)	Mean Na (mg/l)	sd	Mean Na ($\mu g/cm^2$)	Mean Na ($\mu g/cm^2/h$)
1	*1*	10.3	10.8	10.5	10.5	0.26	43.8	43.8
3	*2*	10.1	5.48	7.77	7.70	2.30	32.4	16.2
24	*21*	36.9	24.9	30.9	30.9	5.99	129	5.9
72	*48*	38.4	24.9	31.6	31.6	6.75	132	2.8
120	*48*	30.3	22.5	26.4	26.4	3.89	110	2.3
168	*48*	33.5	20.2	26.9	26.9	6.65	112	2.3
216	*48*	26.1	19.5	22.8	22.8	3.31	94.8	2.0
Total Na leached out		0.098g			156.8			

Table 5 cumulative leaching of K as function of time (renewable tank leaching test) for 100% OPC +0%PFA or 0%GGBFS)50mm cubes

Total duration of immersion of OPC block in leachant (DI water) (hours)	Time between tests (duration of leachant in tank) (hours)	Tank 1 K (mg/l)	Tank 2 K (mg/l)	Tank 3 K (mg/l)	Mean K (mg/l)	sd	Mean K ($\mu g/cm^2$)	Mean K ($\mu g/cm^2/h$)
1	*1*	64.0	63.0	63.5	63.5	0.50	265	265
3	*2*	48.6	39.0	43.8	43.8	4.8	182	182
24	*21*	152	135	144	144	8.5	598	27.2
72	*48*	151	133	142	142	8.9	592	12.3
120	*48*	117	116	117	117	0.45	487	10.1
168	*48*	121	100	111	111	11	461	9.6
216	*48*	90.9	92.5	91.7	91.7	0.80	382	8.0
Total K leached out		0.446g			713		2967	

Table 6 cumulative leaching of Al (at varied time (renewable tank leaching test) for 100% OPC +0%PFA or 0%GGBFS)50mm cubes

Total duration of immersion of OPC block in leachant (DI water) (hours)	Time between tests (duration of leachant in tank) (hours)	Tank 1 Al (mg/l)	Tank 2 Al (mg/l)	Tank 3 Al (mg/l)	Mean (mg/l)	sd	Mean ($\mu g/cm^2$)	Mean Al ($\mu g/cm^2/h$)
1	*1*	0.01	ND	0.01	0.07	0.02	0.29	0.29
3	*2*	ND	0.04	0.08	0.04	0.038	0.17	0.09
24	*24*	0.26	0.47	0.63	0.45	0.189	1.88	0.09
72	*48*	0.75	0.71	0.77	0.74	0.030	3.08	0.06
120	*72*	0.79	0.66	0.96	0.80	0.151	3.33	0.07
168	*96*	1.02	0.71	0.68	0.80	0.187	3.33	0.07
216	*120*	1.05	0.81	1.1	0.99	0.152	4.13	0.09
Total Al leached out		2.43x10-3g			3.89			

Table 7 Cumulative leaching of Cl at varied time in (renewable tank leaching test) for (100% OPC +0%PFA or 0%GGBFS) 50mm cubes

Total duration of immersion of OPC block in leachant (DI water) (hours)	Time between tests (duration of leachant in tank) (hours)	Tank 1 Cl (mg/l)	Tank 2 Cl (mg/l)	Tank 3 Cl (mg/l)	Mean Cl (mg/l)	Sd	Mean Cl ($\mu g/cm^2$)	Mean Cl ($\mu g/cm^2/h$)
1	*1*	0.670	0.815	0.742	0.742	0.072	3.090	3.09
3	*2*	0.099	0.078	0.088	0.085	0.010	0.368	0.18
24	*21*	0.437	0.437	0.437	0.437	0	1.820	0.09
72	*48*	0.390	0.390	0.390	0.390	0	1.625	0.03
120	*48*	0.353	0.353	0.353	0.353	0	1.470	0.03
168	*48*	0.008	0.008	0.008	0.008	0	0.033	7x10-4
216	*48*	0.012	0.012	0.012	0.012	0	0.05	10x10-4
Total Cl leached out		1.3 x 10-3g						

Table 8 cumulative leaching of sulphate as function of time (renewable tank leaching test) for (100% OPC +0%PFA or 0%GGBFS) 50mm cubes

Total duration of immersion of OPC block in leachant (DI water) (hours)	Time between tests (duration of leachant in tank) (hours)	Tank 1 SO_4 (mg/l)	Tank 2 SO_4 (mg/l)	Tank 3 SO_4 (mg/l)	Mean SO_4 (mg/l)	sd	Mean SO_4 ($\mu g/cm^2$)	Mean SO_4 ($\mu g/cm_2/h$)
1	*1*	8.56	9.82	9.19	9.19	0.62	38.30	38.3
3	*2*	3.11	0.00	1.55	1.56	1.55	6.48	3.24
24	*21*	2.78	0.00	1.39	1.39	1.38	5.79	0.28
72	*48*	3.71	0.00	1.85	1.85	1.85	7.74	0.16
120	*48*	3.07	2.68	2.87	2.87	0.19	12.00	0.25
168	*48*	2.47	1.05	1.75	1.76	0.71	7.33	0.15
216	*48*	1.06	1.49	1.27	1.27	0.21	5.32	0.11
Total SO_4 leached out		0.012g			19.89		82.9	

Table 9 cumulative leaching of NO_3 (n-3) at varied time (renewable tank leaching test) for (100% OPC +0%PFA or 0%GGBFS) 50mm cubes

Total duration of immersion of OPC block in leachant (DI water) (hours)	**Time between tests (duration of leachant in tank) (hours)**	**Tank 1 NO_3 (mg/l)**	**Tank 2 NO_3 (mg/l)**	**Tank 3 NO_3 (mg/l)**	**Mean NO_3 (mg/l)**	**sd**	**Mean NO_3 ($\mu g/cm^2$)**	**Mean NO_3 ($\mu g/cm^2/h$)**
1	*1*	13.62	13.06	13.34	13.34	0.28	55.6	55.6
3	*2*	6.93	5.70	6.32	6.32	0.61	26.3	13.2
24	*21*	24.79	31.11	27.95	27.95	3.1	116	5.5
72	*48*	44.93	33.88	39.40	39.40	5.5	164	3.4
120	*48*	43.47	40.62	42.04	42.05	1.4	175	3.6
168	*48*	44.03	21.75	32.89	32.89	11	137	2.9
216	*48*	23.46	32.12	27.79	27.79	4.3	116	2.4
Total NO_3 leached out		0.119g						

Table 10 Cumulative leaching of Na at varied time during tank leaching test (50% OPC + 50% GGBFS 50mm cube)

Total duration of immersion of OPC block in leachant (DI water) (hours)	Time between tests (duration of leachant in tank) (hours)	Tank 1 Na (mg/l	Tank 2 Na (mg/l)	Tank 3 Na (mg/l)	Mean Na (mg/l)	sd	Mean Na ($\mu g/cm^2$)	Mean Na ($\mu g/cm^2/h$)
1	*1*	18.8	15.5	14.7	16.3	2.15	68.0	68
3	*2*	11.8	7.70	7.58	9.02	2.39	37.6	19
26	*24*	35.4	28.2	25.3	29.6	5.21	123	5.9
72	*48*	34.1	25.0	18.4	25.8	7.90	108	2.2
120	*72*	16.5	12.9	10.6	13.3	2.98	55.5	1.2
168	*96*	10.5	8.22	8.47	9.05	1.22	37.7	0.8
216	*120*	6.07	5.79	5.70	5.85	0.19	24.4	0.5
total		0.068g			108.8		453.5	

Table 11 Cumulative release of K at varied time during tank leaching test (50% OPC + 50% GGBFS 50mm cube)

Total duration of immersion of OPC block in leachant (DI water) (hours)	Time between tests (duration of leachant in tank) (hours)	Tank1 K (mg/l)	Tank2 K (mg/l)	Tank 3 K (mg/l)	Mean K (mg/l)	sd	Mean K ($\mu g/cm^2$)	Mean K ($\mu g/cm^2/h$)
1	*1*	45.1	33.8	20.5	33.1	12.3	138	138
3	*2*	28.8	17.8	11.0	19.1	9.0	80.0	40.0
24	*24*	86.8	64.9	37.9	63.2	24.5	263	12.5
72	*48*	83.8	57.8	30.3	57.3	26.7	239	4.98
120	*72*	40.3	30.8	18.3	29.8	11.0	124	2.58
168	*96*	25.9	18.8	14.5	19.7	5.8	82.2	1.71
216	*120*	14.8	14.5	10.1	13.1	2.6	54.7	1.14
total leached out	0.147 g				235.3		980.5	

Table 12 Cumulative leaching of Cl at varied time during tank leaching test (50% OPC + 50% GGBFS 50mm cube)

Total duration of immersion of OPC block in leachant (DI water) (hours)	Time between tests (duration of leachant in tank) (hours)	Tank 1 Cl (mg/l)	Tank 2 Cl (mg/l)	Tank 3 Cl (mg/l)	Mean Cl (mg/l)	sd	Mean Cl ($\mu g/cm^2$)	Mean Cl ($\mu g/cm^2/h$)
1	*1*	1.22	0.45	0.31	0.65	0.49	2.74	2.74
3	*2*	0.24	0.19	0.46	0.29	0.14	1.23	0.615
24	*24*	0.32	0.21	0.12	0.22	0.10	0.90	0.043
72	*48*	0.29	0.12	0.05	0.15	0.12	0.63	0.013
120	*72*	0.09	0.06	0.05	0.07	0.02	0.27	5.6 x 10-3
168	*96*	0.06	0.14	0.04	0.08	0.06	0.30	6.3 x 10-3
216	*120*	0.14	0.75	0.33	0.41	0.31	1.70	0.035
total leached out	1.16 x10-3 g				1.87		7.79	

Table 13 Cumulative leaching of nitrate at varied time during tank leaching test (50% OPC + 50% GGBFS 50mm cube)

Total duration of immersion of OPC block in leachant (DI water) (hours)	**Time between tests (duration of leachant in tank) (hours)**	Tank 1 NO_3 (mg/l)	Tank 2 NO_3 (mg/l)	Tank 3 NO_3 (mg/l)	Mean NO_3 (mg/l)	sd	Mean NO_3 ($\mu g/cm^2$)	Mean NO_3 ($\mu g/cm^2/h$)
1	*1*	27.9	24.4	15.3	22.5	6.52	93.9	93.9
3	*2*	14.5	10.8	6.48	10.6	4.00	44.2	22.1
24	*21*	43.1	30.2	18.8	30.7	12.1	127.8	6.08
72	*48*	40.7	2.53	13.5	18.9	19.7	78.9	1.64
120	*48*	19.5	11.3	8.07	13.0	5.91	54.0	1.13
168	*48*	12.4	8.36	5.64	8.79	3.38	36.6	0.76
216	*48*	8.13	9.54	3.98	7.21	2.89	30.1	0.63
total leached out	0.0698 g, 69.8 x10-3 g				111.7		465.5	

Table 14 cumulative leaching of Sulphate at varied time during tank leaching test (50% OPC + 50% GGBFS ,50mm cube)

Total duration of immersion of OPC block in leachant (DI water) (hours)	Time between tests (duration of leachant in tank) (hours)	Tank 1 SO_4 (mg/l)	Tank 2 SO_4 (mg/l)	Tank3 SO_4 (mg/l)	Mean SO_4 (mg/l)	sd	Mean SO_4 ($\mu g/cm^2$)	Mean SO_4 ($\mu g/cm^2/h$)
1	*1*	9.06	7.43	8.11	8.20	0.81	34.2	34.2
3	*2*	2.14	2.06	2.08	2.10	0.03	8.74	4.37
24	*24*	2.10	2.58	2.97	2.55	0.43	10.6	0.50
72	*48*	1.86	1.52	1.32	1.56	0.27	6.10	0.13
120	*72*	1.49	1.53	1.24	1.42	0.15	5.90	0.12
168	*96*	1.67	2.01	1.49	1.72	0.26	7.17	0.15
216	*120*	2	2.11	1.49	1.86	0.32	7.78	0.16
total leached out	0.012g ,or 12X 10-3 g				19.4		80.5	

Table 15 Pb release during tank leaching test (75% OPC and 25% GGBFS 50mm cube)

Total duration of immersion of OPC block in leachant (DI water) (hours)	Time between tests (duration of leachant in tank) (hours)	Tank 1 Pb (mg/l)	Tank 2 Pb (mg/l)	Tank 3 Pb (mg/l)	Mean Pb (mg/l)	sd	Mean Pb ($\mu g/cm^2$)	Mean Pb ($\mu g/cm^2/h$)
1	*1*	0.183	0.173	0.178	0.178	0.005	0.741	0.74
3	*2*	0.193	0.156	0.175	0.174	0.019	0.727	0.24
26	*24*	0.546	0.364	0.455	0.455	0.091	1.895	0.09
72	*48*	0.475	0.184	0.329	0.300	0.145	1.370	0.03
120	*72*	0.225	0.094	0.159	0.159	0.065	0.660	0.01
168	*96*	0.092	0.026	0.059	0.050	0.033	0.240	0.01
216	*120*	0.032	0.007	0.019	0.019	0.012	0.082	0.00

Table 16 pH values during tank leaching test (75% OPC and 25% GGBFS)

Total duration of immersion of OPC block in leachant (DI water) (hours)	Time between tests (duration of leachant in tank) (hours)	Tank 1 pH	Tank 2 PH	Tank 3 pH	sd	Mean pH
1	*1*	11.7	11.7	11.7	0.035	11.7
3	*2*	11.7	12.0	11.7	0.005	11.8
26	*24*	12.2	12.3	12.2	0.03	12.2
72	*48*	12.2	12.2	12.2	0.03	12.2
120	*72*	12.1	12.1	12.1	0	12.1
168	*96*	12.0	12.0	12.0	0	12.0
216	*120*	11.6	11.7	11.7	0.075	11.7

Table 17 Ca release during tank leaching test (75% OPC and 25% GGBFS 50mm cube)

Total duration of immersion of OPC block in leachant (DI water) (hours)	Time between tests (duration of leachant in tank) (hours)	Tank 1 Ca (mg/l)	Tank 2 Ca (mg/l)	Tank 3 Ca (mg/l)	Mean Ca (mg/l)	sd	Mean Ca ($\mu g/cm^2$)	Mean Ca ($\mu g/cm^2/h$)
1	*1*	410.2	518.6	464.4	464.4	54.2	1935	1935
3	*2*	557.6	487.6	522.6	522.6	35.0	2178	1089
26	*24*	2099	1823	1961	1961	138	8173	389
72	*48*	2244	1927	2086	2086	158	8693	180
120	*72*	150	1434	1467	1467	33.0	6114	127
168	*96*	967.2	1188	1078	1078	110	4490	94
216	*120*	305.7	565.0	435.4	435.4	130	1814	38

Table 18 K release during tank leaching test (75% OPC and 25% GGBFS 50mm cube)

Total duration of immersion of OPC block in leachant (DI water) (hours)	**Time between tests (duration of leachant in tank) (hours)**	Tank 1 K (mg/)l	Tank 2 K (mg/)l	Tank 3 K (mg/l)	Mean K (mg/l)	sd	Mean K ($\mu g/cm^2$)	Mean K ($\mu g/cm^2/h$)
1	*1*	51.40	42.55	46.97	46.97	4.42	195.7	195.7
3	*2*	30.74	29.83	30.29	30.28	0.46	126.2	63.1
24	*24*	92.27	76.50	84.39	84.38	7.89	351.6	16.7
72	*48*	82.11	76.88	79.50	79.49	2.62	331.2	6.90
120	*72*	51.57	58.30	54.94	54.93	3.37	228.9	4.77
168	*96*	46.68	44.9	45.79	45.79	0.89	190.8	3.98
216	*120*	32.27	30.00	31.14	31.13	1.14	129.7	0.62

Table 19 Na release during tank leaching test (75% OPC and 25% GGBFS 50mm cube)

Total duration of immersion of OPC block in leachant (DI water) (hours)	**Time between tests (duration of leachant in tank) (hours)**	Tank 1 Na (mg/l)	Tank 2 Na (mg/l)	Tank 3 Na (mg/l)	Mean Na (mg/l)	sd	Mean Na ($\mu g/cm^2$)	Mean Na ($\mu g/cm^2/h$
1	*1*	19.62	26.38	23.00	23.00	3.38	95.83	95.8
3	*2*	10.88	16.52	13.70	13.70	2.82	57.08	26.5
24	*24*	38.60	42.62	40.61	40.61	2.01	169.2	8.1
72	*48*	34.40	41.62	38.01	38.01	3.61	158.4	3.3
120	*72*	20.88	31.89	26.38	26.38	5.505	110.0	2.3
168	*96*	18.82	24.60	21.71	21.71	2.89	90.46	1.9
216	*120*	12.19	20.29	16.24	16.24	4.05	67.66	1.4

Table 20 NO_3 release during tank leaching test (75% OPC + 25% GGBFs 50mm cube)

Total duration of immersion of OPC block in leachant (DI water) (hours)	**Time between tests (duration of leachant in tank) (hours)**	Tank 1 NO_3 (mg/l)	Tank 2 NO_3 (mg/l)	Tank 3 NO_3 (mg/l)	Mean NO_3 (mg/l)	sd	Mean NO_3 ($\mu g/cm^2$)	Mean NO_3 ($\mu g/cm^2/h$)
1	*1*	17.15	20.89	19.02	19.02	1.87	79.3	79.3
3	*2*	7.98	11.44	9.71	9.70	1.73	40.4	20.2
24	*24*	40.87	32.87	36.87	36.87	4.00	153..6	7.3
72	*48*	38.47	40.68	39.57	39.57	1.10	164.9	3.4
120	*72*	25.42	22.73	24.07	24.08	1.34	100.3	2.1
168	*96*	16.63	18.33	17.47	17.47	0.85	72.8	1.5
216	*120*	8.584	10.56	9.57	9.57	0.99	39.9	0.8

Table 21 SO_4 release during tank leaching test (75% OPC + 25% GGBFs 50mm cube)

Total duration of immersion of OPC block in leachant (DI water) (hours)	Time between tests (duration of leachant in tank) (hours)	Tank 1 SO_4 (mg/l)	Tank 2 SO_4 (mg/l)	Tank 3 SO_4 (mg/l)	Mean SO_4 (mg//l)	sd	Mean SO_4 ($\mu g/cm^2$)	Mean SO_4 ($\mu g/cm^2/h$)
1	*1*	11.82	17.72	14.77	14.77	2.9	61.53	61.5
3	*2*	3.194	4.502	3.848	3.85	0.65	16.03	8.0
26	*24*	4.449	4.061	4.255	4.26	0.19	17.73	0.84
72	*48*	2.097	2.544	2.321	2.32	0.22	9.66	0.20
120	*72*	1.483	2.160	1.822	1.82	0.33	7.59	0.16
168	*96*	1.380	2.851	2.116	2.12	0.73	8.81	0.18
216	*120*	1.280	2.301	1.791	1.79	0.51	7.46	0.16

Table 22 Cl release during tank leaching test (75% OPC + 25% GGBFS)

Total duration of immersion of OPC block in leachant (DI water) (hours)	**Time between tests (duration of leachant in tank) (hours)**	T1 Cl (mg/l)	T2 Cl (mg/l)	T3 Cl (mg/l)	M (mg/l)	sd	M ($\mu g/cm^2$)
1	*1*	0.275	0.299	0.287	0.287	0.012	1.19
3	*2*	0.054	0.099	0.0765	0.0765	0.025	0.31
26	*24*	0.403	0.424	0.4135	0.4135	0.015	1.7
72	*48*	0.306	0.285	0.295	0.295	0.015	1.235
120	*72*	0.165	0.166	0.165	0.165	0.005	0.68
168	*96*	0.123	0.098	0.1105	0.1105	0.015	0.460
216	*120*	0.036	0.034	0.035	0.035	0.01	0.145

Table 23 cumulative leaching of Na during tank leaching test (70% OPC and 30% PFA 50mm cube)

Total duration of immersion of OPC block in leachant (DI water) (hours)	**Time between tests (duration of leachant in tank) (hours)**	Tank 1 Na (mg/l)	Tank 2 Na (mg/l)	Tank 3 Na (mg/l)	Mean (mg/l)	sd	Mean ($\mu g/cm^2$)	Mean ($\mu g/cm^2/hr$)
1	*1*	77.18	46.3	107.4	77.0	30.5	320.7	320.7
3	*2*	19.69	18.46	36.23	24.8	9.92	103.3	51.7
24	*21*	91.47	82.8	140.6	105	31.2	437.4	20.8
72	*48*	77.03	67.96	79.8	74.9	6.19	312.2	6.6
120	*48*	68.31	61.2	51.2	60.2	8.60	251.0	5.2
168	*48*	35.0	34.9	28.63	32.9	3.66	136.9	2.9
216	*48*	23.18	21.6	18.54	21.1	2.36	87.9	1.8
Total Na leached out		0.25g						

Table 24 K release during tank leaching test (70% OPC and 30% PFA 50mm cube)

Total duration of immersion of OPC block in leachant (DI water) (hours)	**Time between tests (duration of leachant in tank) (hours)**	Tank1 K (mg/l)	Tank2 K (mg/l)	Tank3 K (mg/l)	Mean K (mg/l)	Sd	Mean K ($\mu g/cm^2$)	Mean K ($\mu g/cm^2/h$)
1	*1*	101.3	72.6	155.5	110	42.1	457.6	457.6
3	*2*	23.0	27.5	49.4	33.3	14.1	138.9	138.9
24	*21*	108.3	126.5	190.4	142	43.1	590.6	26.8
72	*48*	89.2	102.2	99.5	97	6.8	404.1	16.8
120	*48*	82.7	90.9	64.3	79.3	13.6	330.6	6.9
168	*48*	44.7	52.9	39.9	45.9	6.5	191.1	4.0
216	*48*	23.1	35.9	30.9	30	6.43	125.1	2.6
Total K leached out		0.36g						

Table 25 cumulative leaching of Al at varied time during tank leaching test (70% OPC and 30% PFA 50mm cube)

Total duration of immersion of OPC block in leachant (DI water) (hours)	**Time between tests (duration of leachant in tank) (hours)**	Tank 1 Al (mg/l)	Tank 2 Al (mg/l)	Tank 3 Al (mg/l)	Mean Al (mg/l)	sd	Mean Al ($\mu g/cm^2$)	Mean Al ($\mu g/cm^2/h$)
1	*1*	0.26	0.11	0.73	0.37	0.32	1.54	1.54
3	*2*	0.02	ND	0.35	0.19	0.21	0.45	0.23
24	*21*	0.28	0.33	1.11	0.58	0.46	2.4	0.11
72	*48*	0.88	0.72	0.61	0.74	0.13	3.07	0.06
120	*48*	1.35	0.99	0.89	1.08	0.24	4.49	0.09
168	*48*	1.15	1.07	1.39	1.2	0.17	5.01	0.10
216	*48*	1.43	1.05	1.23	1.24	0.19	5.15	0.11
Total Al leached out		3.38 x 10-3g						

Table 26 cumulative release of Sulphate at varied time during tank leaching test (70% OPC + 30% PFA 50mm cube)

Total duration of immersion of OPC block in leachant (DI water) (hours)	**Time between tests (duration of leachant in tank) (hours)**	Tank 1 SO_4^{-2} (mg/l	Tank 2 SO_4^{-2} (mg/l)	Tank 3 SO_4^{-2} (mg/l)	Mean SO_4^{-2} (mg/l)	Sd	Mean SO_4^{-2} ($\mu g/cm^2$)	Mean SO_4^{-2} ($\mu g/cm^2/h$)
1	*1*	65.8	21.58	43.68	43.7	22.1	182.0	182.0
3	*2*	3.64	2.49	1.80	2.64	0.93	11.01	5.5
24	*21*	2.12	1.58	3.01	2.24	0.72	9.33	0.44
72	*48*	0.96	0.91	0.88	0.92	0.04	3.82	0.08
120	*48*	0.757	0.77	0.633	0.72	0.08	3.0	0.06
168	*48*	0.669	0.66	0.017	0.45	0.37	1.8	0.04
216	*48*	2.80	0.788	1.794	1.79	1.01	7.47	0.16
Total SO_4 leached out		0.033g						

Table 27 cumulative release of chlorine during tank leaching test (70% OPC + 30% PFA 50mm cube)

Total duration of immersion of OPC block in leachant (DI water) (hours)	**Time between tests (duration of leachant in tank) (hours)**	Tank Cl (mg/l)	Tank Cl (mg/l)	Tank Cl (mg/l	Mean Cl (mg/l)	sd	Mean Cl ($\mu g/cm^2$)	Mean Cl ($\mu g/cm^2/h$)
1	*1*	2.05	1.72	1.8	1.89	0.17	7.85	7.85
3	*2*	1.30	1.49	0.62	1.14	0.45	4.75	2.38
24	*21*	0.62	0.89	0.65	0.72	0.15	3.00	0.14
72	*48*	0.61	0.63	0.71	0.65	0.05	2.72	0.06
120	*48*	0.77	1.14	0.72	0.88	0.23	3.64	0.08
168	*48*	1.15	0.89	1.33	1.12	0.22	4.68	0.10
216	*48*	1.33	1.27	1.30	1.30	0.03	5.41	0.11
Total Cl leached out		4.8 x 10-3g						

Table 28 cumulative leaching of Nitrate at varied time during tank leaching test (70% OPC + 30% PFA 50mm cube)

Total duration of immersion of OPC block in leachant (DI water) (hours)	**Time between tests (duration of leachant in tank) (hours)**	Tank 1 NO_3^- (mg/l)	Tank 2 NO_3 - (mg/l)	Tank 3 NO_3^- (mg/l)	Mean NO_3^- (mg/l)	sd	Mean NO_3^- ($\mu g/cm^2$)	Mean NO_3^- $\mu g/cm^2/h$)
1	*1*	29.2	32.0	30.6	30.6	1.39	127.5	127.5
3	*2*	31.1	31.4	29.2	30.6	1.21	127.3	63.7
24	*21*	30.7	29.1	31.8	30.5	1.35	127.2	6.06
72	*48*	29.5	31.6	28.9	30.0	1.40	124.9	2.60
120	*48*	29.7	29.0	30.0	29.6	0.54	123.1	2.56
168	*48*	30.6	32.2	32.2	31.7	0.91	131.9	2.75
216	*48*	28.5	30.7	29.6	29.6	1.08	123.2	2.57
Total NO_3 leached out		0.133g						

The Replacement of PFA with OPC during leaching tank test with deionised water

Table 29 The replacement of Pb at 10 %PFA +90%OPC

Total duration of immersion of OPC block in leachant (DI water) (hours)	**Time between tests (duration of leachant in tank) (hours)**	Pb (mg/l)	Pb (mg/l)	Pb (mg/l)	M (mg/l)	sd	M ($\mu g/cm^2$)
1	*1*	N/D	0.238	N/D	N/D	0.326	N/D
3	*2*	N/D	N/D	N/D	N/D	0.116	N/D
26	*24*	N/D	0.66	0.439	0.267	0.5016	1.11
72	*48*	0.441	0.307	0.368	0.372	0.067089	1.5
120	*72*	0.0501	0.0714	0.0601	0.060533	0.010657	0.252
168	*96*	N/D	N/D	0	N/D	0.179586	N/D
216	*120*	N/D	N/D	0	N/D	0.320824	N/D

Table 30 The release of Pb at 20 %PFA content +80%OPC

Total duration of immersion of OPC block in leachant (DI water) (hours)	Time between tests (duration of leachant in tank) (hours)	Pb (mg/l) T1	Pb (mg/l) T2	Pb (mg/l) T3	sd	Mean	Mean ($\mu g/cm^2$)
1	*1*	N/D	N/D	N/D	0.21	0.211	0.881
3	*2*	N/D	N/D	N/D	0.003	0.003	0.0125
26	*24*	N/D	0.461	0.1305	0.330	0.330	1.377
72	*48*	N/D	0.0401	N/D	0.069	0.069	0.290
120	*72*	N/D	N/D	N/D	0.2745	0.2745	1.1437
168	*96*	N/D	N/D	N/D	0.083	0.083	0.34
216	*120*	N/D	0.607	N/D	0.651	0.651	2.712

Table 31 pH change during 10% PFA+90%OPC

Total duration of immersion of OPC block in leachant (DI water) (hours)	**Time between tests (duration of leachant in tank) (hours)**	pH1	PH 2	pH3	Mean	sd
1	*1*	12.15	12.09	12.08	12.11	0.038
3	*2*	12.03	12.05	12.01	12.03	0.020
26	*24*	12.37	12.42	12.38	12.39	0.027
72	*48*	12.25	12.23	12.24	12.24	0.010
120	*72*	12.26	12.25	12.31	12.29	0.032
168	*96*	12.2	12.1	12.15	12.18	0.050
216	*120*	11.99	12.09	12.1	12.04	0.061

Table 32 pH change during 20%PFA+80%OPC

Total duration of immersion of OPC block in leachant (DI water) (hours)	**Time between tests (duration of leachant in tank) (hours**	T1 PH	T2 pH	T3 pH	sd	Mean
1	1	11.98	11.83	11.89	0.075498	11.9
3	2	11.82	11.75	11.79	0.035119	11.78667
26	24	12.2	12.21	12.1	0.060828	12.17
72	48	12.24	12.25	12.23	0.01	12.24
120	72	12.05	12.25	12.1	0.104083	12.13333
168	96	11.91	12.11	12	0.100167	12.00667
216	120	11.63	12.01	11.95	0.204287	11.86333

Average release of K and Na during replacement of 10 and 20 % PFA replacement

Table 33 average release of 10% PFA +90%OPC

Total duration of immersion of OPC block in leachant (DI water) (hours)	**Time between tests (duration of leachant in tank) (hours)**	k (mg/l)	K (mg/l)	K mg/l)	Mean (mg/l)	sd	M ($\mu g/cm^2$)
1	*1*	130.89	129	129.95	129.95	1.33	541.4
3	*2*	68.22	67	67.61	67.61	0.86	281.7
26	*24*	124.93	125	124.97	124.97	0.049	520.7
72	*48*	159.74	156	157.87	157.87	2.64	657.8
120	*72*	125.32	123	124.16	124.16	1.64	517.3
168	*96*	69.59	64	66.80	66.80	3.95	278.3
216	*120*	50.62	49	49.81	49.81	1.15	207.5

Table 34 K release during (20 %PFA+80 % OPC)

Total duration of immersion of OPC block in leachant (DI water) (hours)	**Time between tests (duration of leachant in tank) (hours)**	K T1 (mg/l)	K (mg/l) T2	K (mg/l) T3	Mean (mg/l)	sd	M ($\mu g/cm^2$)
1	*1*	76.99	76	76.495	76.5	0.50	318.7
3	*2*	20.34	19.2	19.77	19.8	0.57	82.4
26	*24*	98.99	97	97.995	98.0	1.00	408.3
72	*48*	100.5	99	99.755	99.8	0.76	415.6
120	*72*	90.2	89	89.6	89.6	0.60	373.3
168	*96*	50.52	49	49.76	49.8	0.76	207.3
216	*120*	30.96	29	29.98	30.0	0.98	124.9

Table 35 K release during (30 %PFA+70 % OPC)

Total duration of immersion of OPC block in leachant (DI water) (hours)	**Time between tests (duration of leachant in tank) (hours)**	K T1 (mg/l)	T2 K (mg/l)	T3 k (mg/l)	Mean (mg/l)	sd	Mean ($\mu g/cm^2$)
1	*1*	101.36	72.66	155.48	109.8	42.1	457.6
3	*2*	23.05	27.55	49.44	33.3	14.1	138.9
24	*24*	108.3	126.54	190.38	141.7	43.1	590.56
72	*48*	89.21	102.23	99.5	97.0	6.7	404.1
120	*72*	82.77	90.94	64.31	79.3	13.6	330.6
168	*96*	44.73	52.93	39.91	45.9	6.6	191.1
216	*120*	23.18	35.94	30.94	30.0	6.4	125.1

Na release during PFA replaced OPC

Table 36 Na release during 10 %PFA +90% OPC

Total duration of immersion of OPC block in leachant (DI water) (hours)	**Time between tests (duration of leachant in tank) (hours)**	Na (mg/l)	Na (mg/l)	Na (mg/l)	M (mg/l)	sd	Mean ($\mu g/cm^2$)
1	*1*	74.95	73	74	73.98	0.98	308.2
3	*2*	39.72	38	38.5	38.74	0.88	161.4
24	*24*	88.29	86	87	87.10	1.15	362.9
72	*48*	103.87	100	101	101.62	2.01	423.4
120	*72*	89.67	88	88.6	88.76	0.85	362.9
168	*96*	51.66	49.5	50.1	50.42	1.11	423.4
216	*120*	39.33	38	38.6	38.64	0.67	373.6

Table 37 The release of Na at 20 %PFA +80%OPC

Total duration of immersion of OPC block in leachant (DI water) (hours)	**Time between tests (duration of leachant in tank) (hours)**	Na (mg/l)	Na (mg/l)	Na (mg/l)	Mean (mg/l)	sd	Ns ($\mu g/cm^2$)
1	***1***	77.18	46.3	107.39	77.0	30.5	320.7
3	***2***	19.69	18.46	36.23	24.8	9.9	103.3
24	***24***	91.47	82.82	140.61	105.0	31.2	437.4
72	***48***	77.03	67.96	79.8	74.9	6.2	312.2
120	***72***	68.31	61.2	51.2	60.2	8.6	251.0
168	***96***	35	34.94	28.63	32.9	3.7	136.9
216	***120***	23.18	21.6	18.54	21.1	2.4	87.9